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GULF CANADA LIMITED

RESEARCH AND DEVELOPMENT DEPARTMENT
SHERIDAN PARK, ONTARIO, CANADA

FINAL REPORT

DIESEL AND MIDDLE DISTILLATE QUALITY AND YIELD IMPROVEMENTS

by

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SUMMARY

A secure supply of quality middle distillate for Canadian use in the long term is contingent upon the petroleum refining industry's ability to efficiently balance oil resources against product requirements. The middle distillate pool faces reductions in quality as more heavy and synthetic oils are processed.

The current middle distillate availability was assessed by taking a current sample of IPL crude;

Component	Range	Use	Vol% Yield
Lt. Naphtha	C_5 - 82°C	Motor Gasoline Component	7.68
Hvy. Naphtha	82 - 165°C	Reformer Feed	16.93
Lt. Distillate	165 - 270°C	Low Pour Diesel/Kero./Jet A	20.60
Hvy. Distillate	270 - 370°C	High Pour Diesel/Fuel Oil	16.86
Gas Oil	370 - 560°C	FCCU Feed/Lube Feed/Hvy Fuel	22.45
Residuum	560°C+	Bunker/Asphalt/Coker Feed	11.77

The total quantity of straight run middle distillate available from the sample of IPL crude was 37.46 volume %.

The use of middle distillate for the manufacturing of fuels is influenced by the seasonal contraints imposed by cloud point. The Canadian climate has wide variations in ambient temperature year around and the supply of distillate fuels to the Canadian market requires elaborate blending strategy. The formation of wax in a distillate fuel is undesirable and has to be avoided in the formulation stage. The cloud point or wax appearance temperature is used as the control parameter for the various marketing seasons. The three basic fuels types considered here were Winter (-40°C cloud

pt.), Spring/Fall (-18°C cloud) and Summer (0°C cloud) which cover all the marketing seasons. The blending of these fuels in the case of IPL straight run distillates, was simply a matter of controlling the quantity of heavy distillate (cloud point = +3°C) in the blend. The quantity and quality of crude, under these three seasonal cloud point contraints, utilized for distillate product were;

Fuel	Production vol% on crude	Cetane No.
Winter	21.45	48.5
Spring/Fall	28.22	51.5
Summer	37.46	53.9

The high cetane values of the straight run products from the IPL sample taken for the study, reduced the sensitivity of blends to low cetane blending components. But, despite this, the impact of light cycle oil on the middle distillate pool was investigated both before and after upgrading by hydrotreating.

The use of light cycle oil (LCO) from the FCCU process (typically installed in refineries) increases as distillate demand increases. The FCCU (fluid catalyst cracking unit) is the traditional means of utilizing the crude's gas oil fraction to manufacture motor gasoline. At the same time, this process produces middle distillate boiling range material as a by-product. Based on the IPL crude sample of this work, the following FCCU production model was proposed to determine relative production levels;

			Yield on Crude, vol%	
			Normal	MaxLCO
	[ ]	C_3, C_4	6.4	6.4
GAS OIL FEED	[F]	C_5	2.8	2.8
22.45 vol% of crude >	[C]	LCCG	6.5	6.5
	[C]	HCCG	2.8	1.6
	[U]	LCO	3.7	4.9
	[ ]	HCO+		
	[ ]	Decant	2.2	2.2
	[ ]	Coke	1.3	1.3

The FCCU model considered two boiling ranges for the LCO product, a normal LCO and an extended range LCO which incorporated the a portion of the heavy catalytic cracked gasoline (HCCG). This latter product was termed maximum LCO. Samples of these materials were acquired and subjected to traditional desulphurization processing. This hydrodesulphurization step did not saturate aromatics for improvement of the ignition quality of LCO (cetane numbers of these LCOs were <20), but reduced the sulphur contents to acceptable levels for blending. The effect of low cetane light cycle oil on the pool was significant but the high cetane of the straight run distillates supported complete use of the LCO streams to the limit of cloud point. The fuel blend under the most pressure was the winter fuel, which had no Heavy distillate (Cetane No. = 61) included. The CGSB minimum cetane number is 40 and the winter fuel in the maxLCO blend was just on the edge of the specification. The cloud points of the LCO samples were near -20°C and could only be used to their cloud point blending limits and were not fully utilized in the winter blend (approx. 15% of the LCOs were leftover). It was apparent from the blending that, if the straight run light distillate were of lower cetane value (the future trend), the blending limitation would not have been cloud point, it would

have be cetane number. The improvement of LCO ignition quality (cetane number) was investigated from two approaches;

(a) Use of Diesel Ignition Improver Additive
(b) LCO Upgrading by Hydrogenation

The diesel ignition improver additive (Ethyl DII-3) was applied to winter type fuel blends in which the level of LCO was raised beyond its production ratio to produce a fuels with cetane below 40. The response of these fuels to ignition improver was observed at three treatment levels. A blend with a cetane number of 38 was corrected to a cetane number of 40 with a 0.03 - 0.05 wt % treatment level. However, the correction of cetane by additives is not considered a long term solution, and the hydroprocessing approach was also investigated.

The upgrading of LCO was performed and optimized at high severity to determine ignition quality improvements available from hydroprocessing. In this regard, a minimum commercial space velocity was chosen (0.8) at two pressures, 15 and 20 MPa. The results of screening runs indicated aromatic conversion is favoured by temperature up to 380°C. A parallel Gulf/EMR project defined an optimum for aromatic conversion in treating middle distillate at 385°C. With the combined information of these projects, production run conditions were chosen at 380°C for each of the two processing pressures. Both LCO and MaxLCO feedstocks were treated. The effect of pressure on the cetane value of these LCOs was found to be marginal as the cetane gain was only 3 to 6 numbers going from 15 to 20 MPa hydrotreatment. The 15 MPa products had cetane numbers averaging 37.5 and the 20 MPa products averaged near 42. Therefore,

The treatment pressure requirement would be dependent on the middle distillate pool cetane requirement. The LCO products were blended into the three basic fuel types and total pool quality and quantity was reassessed;

	LCO Blends			MaxLCO Blends	
	Production v% on crude	Cetane No. (15MPa)	(20MPa)	Production v% on crude	Cetane No.
Winter	23.7	45.1	46.4	25.1	43.0
Spring/Fall	31.9	47.0	47.6	34.0	47.8
Summer	41.2	47.9	48.6	42.4	49.0

The upgraded LCOs improved the quality of the blends but the impact is not large owing to the LCO production level and subsequent blending level in the pool. The net result was masked out by the high cetane values of the straight run distillates but does show the net effect of LCO cetane value when compared to the untreated case.

The reprocessing of the HCCG product from the FCCU was evaluated as further means to expand the middle distillate pool. It was demonstrated that HCCG (adjusted for the MaxLCO case) could be successfully treated in one stage of processing to produce a satisfactory jet fuel (B type) in terms of CGSB specifications. The conditions of temperature and space velocity were screened at 10.3 MPa pressure (a distillate desulphurizer pressure) and an optimum based on CGSB requirements was found. A production run was performed at 385°C, 10.3 MPa pressure, and 1.9 LHSV on a commercial catalyst to produce specification jet B. The key to the processing step, again, was aromatic conversion which was optimized to produce a product satisfying CGSB luminometer number and smoke point requirements. The reprocessed HCCG product was also evaluated as a

diesel blending component and with a cetane number of 28, it was found that it could be included in the middle distillate pool to the limit of its production ratio once hydrogenated;

	MaxLCO (10 MPa) Blends		MaxLCO (15/20 MPa) Blends	
	Production v% on crude	Cetane No.	Production v% on crude	Cetane No.
Winter	26.7	40.2	26.7	42.1
Spring/Fall	35.6	41.5	35.6	46.9
Summer	44.0	43.9	44.0	48.2

The cloud point of reprocessed HCCG (<-55) allowed it to be used in any of the seasonal fuels. The impact is most significant on the winter fuel where the cetane approached the specification limit. However, the yield gains are good and expanded the winter fuel yield in particular.

2.0 INTRODUCTION

The Canadian oil refining industry operates in a constantly changing environment of crude supplies and consumer product demand. Balancing supply and demand efficiently, requires flexibility in refining operations and processing strategy. Also indigenous to the Canadian industry is a wide seasonal variation requiring continuous product formulation changes.

The refiner's installed hardware has limited flexibility to meet wide product demand variations. A modern refinery is usually equipped with facilities for:

Distillation - atmospheric
- vacuum

Hydrogenation - HDS/HDN
- hydrorefining
- hydrocracking

Reforming

Catalytic Cracking - FCCU

Alkylation

Coking or Asphalt Production

A schematic for a typical refining operation is given in Figure 2.0.1 and shows the interelations of the above units.

The process design for a given refinery is often based apon a standard or average crude charge and a projected product slate. In most instances, however, the refinery has evolved over a number of years and processing units have been upgraded or added over time. In addition to that, the past few years have seen the penetration of significant amounts of synthetic crudes into the crude supply. At the same time a growth in middle distillate fuel demand has taken place. These changes put strains on refiners with

conventionally based processes, particularly in the production of good quality diesel fuel. The synthetic crude middle distillates making their way into refinery diets are typically aromatic and consequently of low ignition quality, limiting thier usage.

With increased middle distillate demand and declining middle distillate quality, the conventional refiner is faced with a two fold unbalancing of supply and demand and has to either increase the crude run or utilize nontraditional sources of blending components or add a new processing unit (like a gas oil hydrocracker) to return to a balanced situation. The later is an expensive proposition in terms of both capital and operating costs. The increase of crude run produces surpluses of other components and negatively affects operating costs.

The expansion of the middle distillate pool by utilizing other existing process streams remains as the most cost effective option. The Fluid Catalytic Cracking Unit (FCCU) produces streams in the middle distillate boiling range which are often used as blending components for diesel or jet fuels after suitable pretreatment. These, however, are of low ignition quality which limit the extent to which they can be used.

The purpose of the following work was to evaluate the present middle distillate pool size and quality when including FCCU LCO components and to demonstrate improvement of middle distillate ignition quality by use of additives and by LCO upgrading. The reprocessing of Heavy Catalytically Cracked Gasoline (HCCG) was also investigated for the purpose of producing another diesel and/or jet fuel blending component and thus extending the middle distillate pool.

The above approach reflects ongoing concerns for security of supply and efficient utilization of resource. The Canadian diesel fuel quality and availability has been predicted to decline due to decreasing supply of paraffinic sources and the influx of the aromatic sources like synthetic crudes. The ignition quality of the aromatic middle distillate from synthetic crude is relatively poor and generally downgrades the middle distillate pool. The supply option wereby FCCU cycle oil is used to expand the pool also has the effect of downgrading the pool quality as well because of this stream's aromaticity. At the same time, upward pressure on ignition quality for the reductions of combustion emissions is expected. The shortfall in ignition quality caused by all of these factors will inevitably reach the point where upgrading will be required to utilize LCO, or face excluding cycle stock with the resulting product imbalances. Extending crude run to meet demand could possibly lead to dependance on foreign crude supplies.

The work discussed here is useful to the Canadian Refining Industry in that middle distillate yields are assessed, options for expanding the yields are evaluated and limitations are defined.

The specific objectives of this project were:

- characterize typical IPL mixed crude
- characterize typical FCCU Light Cycle Oils (LCO) and HCCG
- hydrogenate LCO to current practise (ie desulphurize)
- hydroprocess LCO to upgrade ignition quality
- blend straight run and treated LCO to make year-round diesel fuels and evaluate the blend impact of the alternate types of LCO products
- evaluate the effect of ignition improver additives
- compare the upgrading and fuel additive approaches
- reprocess HCCG to make a diesel or jet fuel blending component

3.0 EXPERIMENTAL

3.1 Executed Work Statement

The project was divided into five principal tasks and over the course of the work, certain ammendments and changes were made. The following reviews the work statement as the work was carried out.

Task No. 1 Crude Selection, Analysis and Preparation of Distillate Components

(a) A sample of Interprovincial Pipeline mixed crude was obtained (400 L) and analyzed for component yield and properties. The crude was distilled into the following boiling range fractions;

Comp.	Range	Use
Lt. Naphtha	C_5 - 82°C	Motor Gasoline Component
Hvy. Naphtha	82 - 165°C	Reformer Feed
LSR Distillate	165 - 270°C	Low Pour Diesel/Kero./Jet A
HSR Distillate	270 - 370°C	High Pour Diesel/Fuel Oil
Gas Oil	370 - 560°C	FCCU Feed/Lube Feed/Hvy Fuel
VTB.	560°C+	Bunker/Asphalt/Coker Feed

The light and heavy straight run distillates were used in the blending work and were characterized in greater detail by mass spectroscopy.

(b) In addition to the samples of IPL crude, further samples were obtained of FCCU streams. Two different LCO samples were taken to represent seasonal demand adjustments made when LCO is added to the diesel pool. When demand for middle distillate is moderate then a narrow boiling range LCO is produced. In high demand

periods, a wider cut of boiling range is taken off the FCCU fractionator incorporating some lighter material from the HCCG boiling range and is termed in this report as MaxLCO. These samples were collected when the FCCU had a significant Syncrude component in the feed.

The LCO samples were treated in the pilot plant hydrotreater to desulphurize as is done commercially. This involved two treatment severities representing an older style DDS (Distillate Desulphurizer) and a more modern high pressure DDS. The conditions selected, were based on actual Gulf operations. The catalyst used was a Katalco NT-550 which is widely used in industry for DDS service. The processing parameters were;

(i) LHSV = 2.5, Pressure = 4.5 MPa, Temp. = 311°C
(ii) LHSV = 0.8, Pressure = 10.0 MPa, Temp. = 325°C

The hydrogenation runs were performed on catalyst that was sulphided and de-edged. Complete material balances were performed for each treatment run. The products were fully characterized including mass spectroscopy analyses.

This part of task #1 provided blending stocks for the studies in task #3.

Task #2 Upgrading the Ignition Quality of Light Cycle Oil

The two LCO samples (described in task #1), LCO and MaxLCO, were subjected to severe treating to upgrade the ignition quality (ie cetane). The treatments involved optimization of temperature at two pressures, namely 15 and 20MPa. The LHSV of these runs was at level considered a commercial minimum, namely 0.8. The optimization runs represented screening experiments to determine production run

conditions for the four final LCO product blending components which were prepared for the task #3 studies. The catalyst chosen for the treatment work was Katalco NT550.

All runs performed in this task included material balancing and product characterization. The final products were assessed in detail for purposes of the blending study in task #3.

Task #3 Blending of Summer and Winter Grade Diesels and Product Testing

The components prepared in tasks #1 & #2 were used in a blending study where year-round diesel fuel products were formulated. There were three sets of blends prepared in order to evaluate the production scenarios.

Scenario 1: The desulphurized LCO products of task #1b were blended with the straight run (SR) distillates to formulate the three basic types of fuel used year-round in the western region. This was to represent the limitations of current blending practice in order to establish the basic middle distillate pool size before alternatives. The three basic fuels were chosen to be those defined by the cloud points 0,-18, and -40°C which satisfy western region requirements for summer, spring/fall, and winter temperature operability. The following blending design was used:

Component	0°C	-18°C	-40°C
LSRD	X	X	X
HSRD	X	X	
LCO	X	X	X
MaxLCO	X	X	X
	6	4	2

The -40°C cloud point precludes the use of HSRD as a blending component for winter diesel, limiting blends to two; one with LCO & LSRD and the other with MaxLCO & LSRD. The fall/spring fuel blends are comprised of two combinations of LSRD/HSRD with each of the two types of cycle oil. The summer fuel blends are comprised of three combinations of LSRD/HSRD with each of the cylcle oils reflecting the relaxation of cloud point requirements. The LCO and MaxLCO samples used were products of the 10.0 MPa treatment runs representative of modern DDS Unit operation. The blend compositions were further constrained by two other criteria;

(a) CGSB Specifications

(b) Production Ratios

Therefore, the blends were all made to meet CGSB specifications for diesel, respect component production levels, and satisfy the seasonal cloud point requirements.

Scenario 2: A worst case approach was used to evaluate the simultaneous use of LCO's and ignition improvers. A common production problem is the winter fuel supply of low cloud material. The LCO's typically have good low temperature properties and in the winter fuel situation represent a significant portion of the diesel pool. The offsetting factor in LCO use is its relatively poor ignition quality and the most common cure for this is the use of additives for cetane improvement.

The LCO products of task #1b were used to prepare winter grade fuels for studies of the cetane improver effect. The clear cetane numbers of the 4.5 and 10 MPag LCO products blended with LSRD were evaluated. The effects of one cetane improver (Ethyl DII-3, an octyl nitrate) was investigated at three addition levels to generate cetane response curves. This also provided relative

operating cost data for the use of cetane improver. In addition to the cetane measurements, the blends were fully characterized. This work represents an expansion of the original plan to provide more insight into ignition improver response and to compensate for forgone experiments in scenario three, as discussed below.

Scenario 3: The final portion of the blending study was the evaluation of upgraded LCO's produced in task #2. Due to a sample mix-up, two of the hydrotreated products were blended together and the number of blends was reduced from 12 (original plan) to 9. The blending design used was:

Component	0°C	-18°C	-40°C
LSRD	X	X	X
HSRD	X	X	
LCO(15MPa)	X	X	X
MLCO(20MPa)	X	X	X
LCO/MLCO (15/20MPa)	X	X	X
Total Blends	3	3	3

These blends were made using the same criteria as those used in scenario one. All the fuels were fully characterized. The blends in this part of the study represent the upgrading possibilities for LCO as an alternative to the use of additives. The blending limitations to meet diesel fuel requirements were evaluated as well.

Task #4 Reprocessing HCCG for Use in Diesel or Jet Fuel

The work carried out in this task expanded from the original plan to encompass two processing options. The original work plan involved a two stage processing of this FCCU stream. The HCCG

component from the FCCU is typically a low volitility gasoline blending component which is rich in olefins and aromatics. The olefins are undesirable for diesel or jet fuel from product stability and combustion property points of view and need to be saturated. The second goal is the conversion of aromatics to naphthenes required to achieve ignition property improvement. These processing steps were carried out in two stages because the exothermic heat of reaction was thought to be to high to control the hydrogenation system effectively. The first processing option evaluated the two stage approach and provided temperature optimization for each of the two reaction groups. The catalyst used in the pilot plant hydrogenation runs was Katalco NM506. This catalyst was chosen based on indications from a parallel EMR/Gulf project "Improved Synthetic Crude Processing" (6). The pilot plant runs included six temperature conditions at 4 MPa pressure to survey the first stage and four temperature conditions at the second stage pressure of 10 MPa. Two production runs were performed using the survey run temperature optimums for olefin and aromatic saturations, respectively. A third series of survey runs was performed in the evaluation of single stage processing. All survey and production run products were analyzed for composition and boiling point distribution.

Through an ammendment to the original Task #4 work statement the optimization of one stage processing was included later. The work involved obtaining further HCCG feedstock and hydrotreating at the temperature optimum observed in the early program, varying space velocity to produce a specification Jet B. This involved a further four screening runs in the pilot plant hydrotreater using the same catalyst, pressure and optimum conversion temperature as used before. With the aromatic conversion data generated in the survey runs, a production run was made at the optimum space velocity determined by agreement with the EMR S.A. This final product was completly evaluated for combustion properties and composition.

Task #5 Compilation of Monthly and Final Reports and Presentation

This task was to provide monthly progress reports for the ongoing project as well as the final, overall project report. The completion of the technical programme and report in this project was to be followed by a presentation of results at the EMR offices.

3.2 Characterization Methods

All products and samples were characterized using standard ASTM methods and conventions. In addition to these, the latest National Standards of Canada specifications for evaluating the fuel properties were used. The laboratory testing standards are set by a number of organizations and they are:

ASTM - American Society for Testing and Materials
IP - Institute of Petroleum
ISO - International Organization for Standardization
CGSB - Canadian General Standards Board

The national standard specifications for Canadian diesel and jet fuels are included in this report. Supplemental analysis, in particular, mass spectroscopy compositionals are based on Gulf in-house standards which have been extensively supported by experimentation and verification testing. Methods of analyses are quoted throughout the report.

3.3 Experimental Apparatus and Procedure

Apart from the pilot plant equipment all apparatus are standard ASTM type for the petroleum industry. The following is a description of the pilot hydrotreaters used in the execution of the work statement tasks # 1, 2 and 4.

Hydrotreater Unit Description

The three hydrotreater units used in this project are labelled as P-12, P-16, and P-17(DH). All the units have basic similarities in design and operation and only differ in catalyst bed capacity. With the exception of P-16, the units are of the recycle gas type and operate essentionally isothermally. P-16 is a once through gas design. The unit capacities and limitations are listed below and P&ID's are shown in figures 3.3.1, 2, and 3.

Unit No.	Max. Catalyst Charge	Pressure Limit	Temperature Limit
P-12	325 ml	34 MPa	420°C
P-16	200 ml	20 MPa	420°C
P-17	1500 ml	20 MPa	390°C

The hydrotreaters are equipped with feedstock and hydrogen metering devices as well as product collection and stabilization facilities. The reaction systems are comprised of a inline feedstock preheater followed by a reaction vessel heated along its length by external resistance heating. The reactor effluent is passed through a heat exchanger to separation vessels to remove reaction gas for either recycling and/or purging. The recycled gas systems include an online process gas chromatograph and all reaction systems have provision for offgas sampling. The offgas sampling along with feed and product metering imformation allow complete and accurate material balancing of each of the units' operation. Temperatures are controlled by feedback type controllers and records of catalyst bed temperature profile are taken by a data logger on one minute cycles. The temperature profile is obtained by a multipoint thermowell and thermocouple arrangement. The pressure is controlled by a back pressure relief system. Inlet gas pressure is adjusted

above the unit pressure until a desired flow level is achieved. The liquid feed is metered into the reaction system by a positive displacement type pump.

Pilot Plant Operating Procedure

The operation of the hydrotreating pilot plants include unit preparation for catalyst charging, catalyst bed placement, unit pressure testing, as well as startup, shutdown and emergency procedures.

A typical pilot plant run involves reaction vessel cleaning to remove previous run deposits followed by catalyst charging. With catalyst bed in place the reaction system is thoroughly checked for pressure leaks at one and a half times the operating pressure. The

pilot run can then commence starting with establishment of the operating pressure and the gas recirculation rate is set at the operating requirement. The system is then warmed up to 150°C and held for a 24hr catalyst drying period (only with freshly charged catalyst). If the catalyst charge is new, it may require presulphiding and this operation is described below. The liquid feed is subsequently started at the specified rate and levels are established in the product separators. The reactor temperature is then raised at 25°C/hr until 320°C is reached, then at 10°C/hr increments until the reaction temperature is obtained. The unit is then operated until at least five reactor volumes of product have been processed before the unit is considered lined out. The lineout completion is also checked by product gravity consistency or other characteristics, as desired.

The unit is continuously monitored by operating personal and hourly

or bihourly log readings are taken. A sample log sheet is shown in Figure 3.3.4.

The unit is shutdown by reducing the reactor temperature to 150°C, at which point the feed is stopped and catalyst bed is flushed with solvent. The gas flow through the reactor is stopped shortly after flushing, followed by either blocking the reaction system at pressure or by depressurizing and catalyst removal, if the run series is completed.

Catalyst Presulphiding Procedure and Example

The sulphiding of the catalysts used in this study was carried out according to a standard procedure, which is outlined as follows:

- The reactor was charged with sieved and dried catalyst in the arrangement specified for each reaction system used.
- The reactor was subsequently pressure tested using H_2 at 27.6 MPag until a leakage rate below 14 kPa/hr was reached.
- The reactor was warmed up to 150°C and H_2 purged to dry the catalyst.
- A hydrofined middle distillate, spiked with 6000 ppm sulphur, was used as the presulphiding medium. The system was warmed up to 300°C at 28°C/hr with a feedrate equivalent to one space velocity. The gas rate was set at 890 L/L with a minimum of 93% H_2 in the gas.

- Presulphiding was carried out at 20.7 MPa pressure and 1.0 LHSV. These conditions were maintained until the prescribed amount of sulphur had been passed over the catalyst. The time required to complete the operation was estimated as given below. The indicator used for marking sulphiding completion was the breakthrough of H_2S in the recycle gas. Each H_2S breakthrough was followed by a temperature increase of 30°C until 390oC was reached.

- The manufacturers's specifications were used to determine the percentage of sulphur added to the catalysts.

- The H_2S concentration in the effluent gas was monitored for two hours after the final breakthrough to ensure that sulphiding was complete

<u>Example Calculation</u> (e.g. Katalco NM506)

Feedrate = catalysts charge x LHSV
= 0.323 L x 1.0
= 0.323 L/hr

Weight of Catalyst = catalyst charge x bulk density
= 0.323 x 920 g/L
= 297.2 g

NM506 metals Ni@ 5.3wt% x 297.2 g = 15.8 g = 0.27 gmoles Ni
Mo@ 18.0wt% x 297.2 g = 53.5 g = 0.56 gmoles Mo

Sulphiding reactions: $3Ni + S_2 <-> Ni_3S_2$
$Mo + S_2 <-> MoS_2$

Moles of S_2 required = 0.27/3 + 0.56 = 0.65 gmoles
= 41.7 g S2

Amount of CS_2 required = MW CS_2/MW S_2 x Sulphur required
= 76.131/64.128 x 41.7
= 49.5 g CS_2

Quantity of feed required = CS_2 required x 1/spike concentration
= 49.5 x 1/6000ppm
= 8.3 kg feed

Time required to complete sulphiding of NM506 catalyst at 1 LHSV
= feed required x 1/sg feed x 1/LHSV
= 8.3 kg x 1/0.8644 x 1/0.323
= 29.7 hr

4.0 RESULTS AND DISCUSSION

4.1 Task #1 Crude Selection, Analysis and Preparation of Distillate Components

The crude selected for the project was a current sample of the Interprovincial Pipeline mixed crude representing a mix of crudes collected from oil fields throughout western Canada. The IPL blend has some synthetic crude in its make-up but is primarily comprised of conventional production. The sample was taken in July of 1983 and represents a "snapshot" of current production and of feedstock available to Canadian refineries for the production of fuels. The crude was distilled into the basic fractions for product manufacture as listed below;

Fraction	Boiling Range	Volume Yield %	Uses
LSR Naphtha	15 - 75°C	7.68	Gasoline Blending
HSR Naphtha	75 - 165°C	16.93	Reformer Feed
LSR Distillate	165 - 270°C	20.60	Low Pour Diesel, Kerosene, Jet A
HSR Distillate	270 - 370°C	16.86	High Pour Diesel, Fuel Oil
Gas Oil	370 - 560°C	22.45	Feed for Lubes/FCCU
Vacuum Tower Bottoms	560°C+	11.77	Bunker or Feed for Asphalt/Coker or FCCU

The boiling ranges of the above fractions were selected to represent a general case for a possible future refinery operation adjusted for maximum middle distillate production.

The LSRD and HSRD cuts were characterized and analysis is shown in table 4.1.1. Data in this table show that the clear cetane of these distillates is very high. As a result, relatively higher amounts of low cetane blending components could be accepted. This ignition quality was not expected in the design of the experimental work, as cetane numbers for the straight run distillates are typically lower. The compositional data shows that these distillates are of low aromaticity and of high paraffin content which explains the measured cetanes. Normal paraffins contribute significantly to cetane ignition quality followed by a moderate contribution made by naphthenes.

The cetane number is an inverse measure of ignition delay in diesel combustion where the only source of ignition is by compression of the fuel. This, of course, is the direct inverse of the octane number property measured on gasoline samples where compression ignition is undesirable. Consequently the fuel formulation in gasoline requires high aromaticity. This crude, however, contains very lean SR naphtha, that is a naphtha with low aromatics content and would pose some difficulty to the refiner with octane demand. The paraffinic nature of this crude is again reflected in the naphtha composition (see the crude assay in appendix 1).

The boiling range overlap in naphtha and middle distillate products poses some problems here. Aromaticity is dersirable for gasoline manufacturing but not for diesel; (normal) paraffinicity is desirable for for diesel manufacturing but not for gasoline. The IPL sample analyzed in this work was a very favourable diesel/middle distillate source owing to its paraffinic nature. Expanding the boiling range on middle distillate from this crude is as not detrimental to cetane ignition quality as it is on other crudes. If the long term projections of higher aromaticity are

realized, then the widening of the middle distillate cut range may have impact on lowering cetane quality.

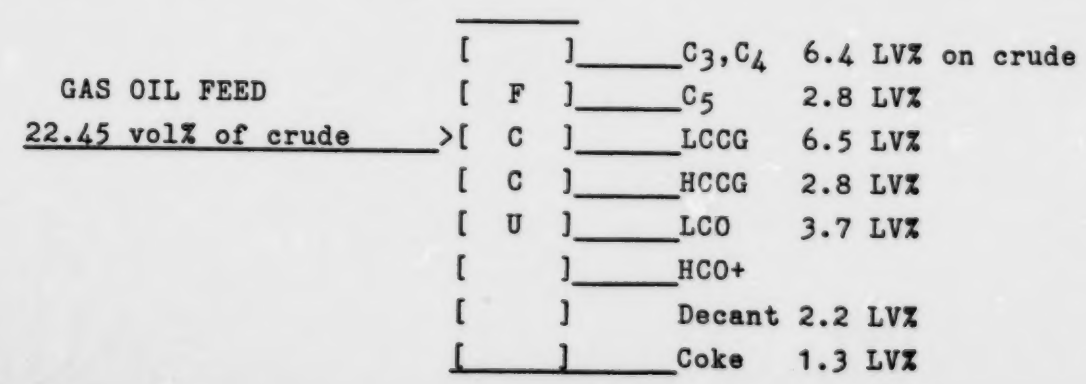
Based on the straight run yields in this crude, the distillate available for fuel is 37.5 volume% of crude and the distillate available for gasoline (after a 90 volume % reformer yield) with back blending of butanes would be approximately 25.8 volume% on crude. Utilization of the gas oil fraction is important to balance the production of fuels against the demand. The FCCU process is typically used to convert gas oil into gasoline blending components to make up the shortfall in straight run gasoline.

The FCCU and LCO Production

The demand for gasoline, since the mass production of the automobile has traditionally been higher than that of diesel fuel and in order to supply that demand there was a need to go beyond the straight run proportions of these fuels in the crude. The catalytic cracking process was developed to utilize the the gas oil fraction to produce further gasoline blending components. Many developments and improvements have been made in catalysts and processes which have lead to todays high conversion FCCU's.

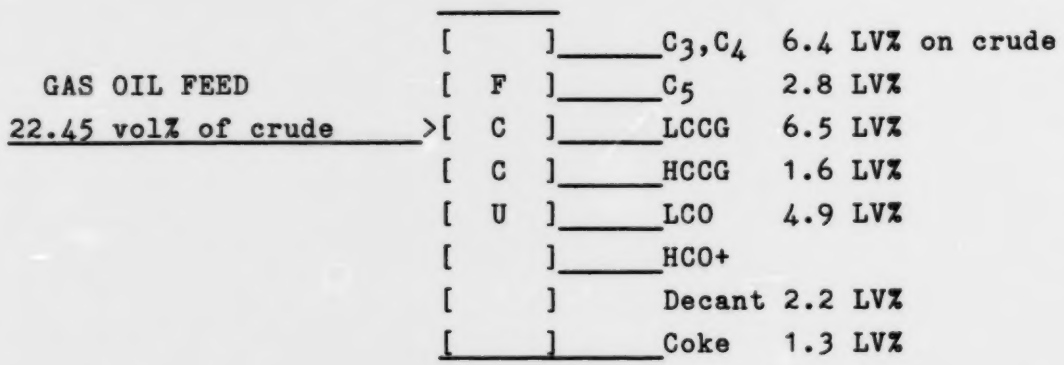
The FCCU can produce a variety of products depending on the feed, catalyst and operating conditions selected. General material balances are given below as examples. Also shown are the product streams associated with the FCCU.

Average Operation



Maximum LCO

The FCCU product fractionator can be adjusted in most cases to a maximum LCO mode where the tail end of the HCCG is included in the LCO fraction



The FCCU produces a wide range of products, as shown, and the examples given are typical for a fuels operation. The product streams utilized in gasoline manufacturing are the C_3/C_4 (olefinic feed for oligomerization processing then to gasoline pool), the C_5, the Light Catalytically Cracked Gasoline (LCCG), and HCCG streams. The LCO stream has multiple uses as a low pour diesel blending component, as a home heating fuel, flux for asphalt, speciality products like drilling fluid or as a cut back for bunker fuels. The HCO and decant streams are often sent to bunker blending. Because of the boiling range of HCCG and LCO, however, these streams are acceptable as sources for diesel and possibly jet fuel blending components. These are useable only after suitable pretreatment has been performed and the extent or severity of treatment depends on the quality of the straight run blending components to be used and their concentration in the final product. For the purpose of demonstrating maximum middle distillate yield and the resultant quality, the samples of typical FCCU streams, namely LCO and HCCG, were included. The LCO and maximum LCO samples, as described above, were characterized (see Table 4.1.3). The LCO and MaxLCO differ only in that the last 30°C of the HCCG

boiling range was added to a subsample of the LCO in proportion to the production ratios. The result is an increase in the quantity of monoaromatics, decrease in density and in the cetane number in the MaxLCO. The cetane numbers of the LCO and MaxLCO were not measureable by ASTM procedure because the cetane was lower than the reference fuel used to rate the samples. Instead, the cetane index (CGSB) had to be calculated. It was apparent that these components are going to have negative affects on any blends in which they are used. The HCCG remaining from the MaxLCO synthesis became the HCCG used for the reprocessing study. It should be noted that there were actually two samples used in the study owing to the redefinition of task #4 and therefore two analyses are shown in Table 4.1.2. The HCCG, like the LCO samples, are highly aromatic and consequently are also of low diesel ignition quality.

The HCCG samples, when evaluated as gasolines, were found to have octane numbers around 85 which is sufficient for use in regular leaded gasoline. But because the octane and cetane numbers are inverse properties, it is not suprising that the cetane numbers of these samples are less than 20 (ASTM D-613) vs the CGSB specification of 40 C.N.

Upgrading of HCCG is discussed in task #4.

LCO Desulphurization

The LCO samples obtained in this study were taken from a FCCU fractionator, while in a normal operation the LCO streams are hydrogenated to saturate olefins and to desulphurize. In this regard, the work statement included provision to treat the LCO's in a typical fashion. Commercially, a wide range of hydrogenation severities are utilized, and hence these were simulated in the pilot plant treatment of the samples. The two treatment severities used in the project were ;

- o LHSV = 2.5, Pressure = 4.5 MPa, Temperature = 311°C
- o LHSV = 0.8, Pressure = 10.0 MPa, Temperature = 325°C

These conditions performed with commercial NT550 Katalco catalyst were intended to simulate each of an older style and of a more modern high pressure DDS Units. By treating the LCO in this way, the current middle distillate pool quality could be assessed (task #3) when operating in the maximum distillate mode.

The pilot plant treatment runs are summarized in tables 4.1.5 and 4.1.6 where material balances and product analyses are given. Table 4.1.5 shows the LCO and MaxLCO runs at 4.5 MPa and 4.1.6 shows the LCO and MaxLCO runs at 10.0 MPa. Table 4.1.4 gives the Katalco NT550 catalyst properties. The low pressure runs at 4.5MPa were very mild and is reflected by slight compositional change. Only the triaromatics were affected and a 50% reduction had taken place; little, if any, dealkylation occurred. Also, the amount of sulphur removed was only about 50%. This is typical of this low severity (older style) unit operation; especially at 2.5 LHSV. As a consequence of not having saturated any significant amount of aromatics, the cetane number of the final product was still too low to be measured, i.e. less than 20. These LCO products were the components of the worst case blending scenario for task #3, where diesel ignition improvers were evaluated. The 4.5 MPa pressure products will affect the straight run blending components the most adversely in ignition quality. The conditions of this mild treatment are used commercially in a few instances for cases were sulphur is low and the primary objective is stabilizing any degradeable double bonds like higher order olefins. If the straight run distillates in which these LCOs are to be blended are low in in sulphur and more could be tolerated in the LCO. Hence only mild desulphurization is required. The CGSB specification for sulphur in diesel is 0.7 wt% were as the 4.5 MPa products were 0.5wt% and the LSRD/HSRD products were 0.36wt%. However, these would not be

suited for blending Jet A (0.2 wt% max.). It should be noted that these sulphur levels may be revised to reflect more stringent emission requirements.

The runs performed at the 10.0 MPa pressure and lower LHSV (0.8) produced products with more noticable molecular changes. Significant reduction of tri- and di- aromatics had taken place. The tri-/di- aromatic reduction is most likely the saturation of an outer ring of the multi-ring aromatic. Actually, not much in the way of hydrocracking can be expected at the temperature of operation (325°C) Some monoaromatic saturation was apparent though as shown by the increase in cycloparaffin content. These changes had the effect of improving the cetane quality into the measurable range (approx. 22 - 23 cetane) and a significantly better sulphur removal was achieved. In total, the higher pressure/lower space velocity combination improves the operation effectiveness and the LCOs produced are representative of more up to date processing. These LCO products were therefore used to represent the present LCO blending stock in the diesel fuel evaluation in task #3. More discussion on distillate hydrotreating is given in task #2.

Approximate Crude and FCCU Gasoline Yield

Although this study is aimed at middle distillate production, the relative quantity of gasoline produced is of interest. The gasoline: middle distillate production ratio is of particular interest when evaluating diesel supply scenarios. This relates to the efficiency of crude utilization. The examples of FCCU operation and the widening of the middle distillate boiling range shown here indicated that the amount of material available for fuels production can be enlarged (pending the evaluation of quality, task #3). The gasoline pool was reduced by the widening of boiling range and the redirection of HCCG. Based on the average FCCU case and

this IPL crude, the total becomes 44 vol% for gasoline vs. 41 vol% for middle distillate (including LCO:excluding HCCG). In the maximum LCO mode the gasoline pool would be 43 vol% vs 42 vol% for middle distillate (vol% on crude). And finally, in case where HCCG is reprocessed, the gasoline pool becomes 42 vol% of the crude and middle distillate becomes 43 vol% of crude. At this point the long term projection of 1:1 gasoline:middle distillate production ratio could be satisfied. However, product quality considerations have yet to be addressed (task #3).

4.2 Task #2 Upgrading the Ignition Quality of Light Cycle Oil

Both the LCO and MaxLCO samples, analyzed in task #1, were subjected to further processing in order to demonstrate the improvement in LCO combustion properties achievable by severe hydroprocessing. To do this, a pilot plant campaign was initiated to explore the effects of temperature on each of the LCO samples at two different operating pressures. Based on the results produced in these screening runs, optimum conditions were chosen for production runs on each of the LCO samples. The pressures chosen were 15 and 20 MPa which represent operating severity much beyond that used conventionally and these pressures would require a significant capital investment. However, as middle distillate quality diminishs due to changes in demand or in crude slate, the high pressure hydroprocessor will become more common. The light cycle oil stream approachs a worst case treatment owing to the high aromaticity of these oils (above 75wt%). The use of LCO as a blending component in diesel fuel requires careful consideration of blend concentration and straight run distillate quality. The fuel qualities which need to be addressed when evaluating blending potential are;

- cetane no. / smoke pt.
- cloud pt / pour pt.
- residue / thermal stability
- viscosity

In its unprocessed state, LCO has very poor combustion properties (ie cetane number for diesel, smoke point for jet fuel) and often has poor thermal stability in that residues can be formed by heating (due to unsaturates). However, as a blending component (especially in winter) LCO has supeior cloud/pour point quality and viscosity as an offset for paraffinic straight run components. When LCO is used and a shortfall in cetane number occurrs, then a cetane improver is used. Low concentrations have been used traditionally and usually just to pass marginal fuel blends for sale. The decline of quality in the straight run pool, to the point where a large cetane shortfall occurs, may not be rectified by additives economically. Also, high additive concentration may cause high residues to occur. In these situations, hydroprocessing is more attractive.

The LCO feedstock is approximately 75 % aromatics, 12 % paraffins, 8 % cycloparaffins and 5 % aromatic sulphur compounds (thiophenes etc.). The contribution made by each of the molecular groups to cetane varies from low for aromatics to moderate from cycloparaffins to high from paraffins. The molecular change desired in LCO processing is therefore aromatic conversion. From literature, an approximate hierarchy of hydroprocessing reactions by severity is outlined. As severity increases, the following reactions occur:

- Olefin Saturation
- Heteroatom removal
  - sulphur and nitrogen removal (HDS, HDN)
    e.g. thiophenes: single ring followed by di- and tri- etc.

- Aromatic Saturation
  - polynuclear aromatics first and increasing severity to monoaromatics
- Hydrocracking
  - alkyl side chains
  - scission of multi-ring cycloparaffins
  - paraffins
  - scission of multi-ring aromatics
  - ring opening

The mild treatment runs discussed in task #1, particularly the 10 MPa pressure runs, achieved the HDS/HDN reactions but only marginal levels of aromatic saturation. The increase in operating pressure used in this task was to provide the aromatic saturation reactions as the means of improving the cetane quality of the LCO samples. The hydrocracking reactions, in the context of middle distillate production, are undesireable because they can reduce the yield in the middle distillate boiling range. Some of these reactions occur,to some extent, at the same severity as the majority of aromatic saturation reactions. The processing involves a compromise between the maximization of aromatic saturation and minimization of hydrocracking to naphtha or light ends. The result of aromatic saturation is the improvement of cetane quality by virtue of cycloparaffins increase. The severity necessary to produce paraffins from LCO (and hence the greatest cetane gain) would also cause excessive middle distillate volume losses.

Therefore the objective of the processing condition selection was to vary operating temperature at the two pressure levels (at a fixed LHSV = 0.8) to achieve maximum aromatic conversion and minimum naphtha production. The treatment catalyst used for the pilot plant work was again Katalco NT550 (catalyst properties are given in Table 4.1.2).

The treatment runs are summarized in Tables 4.2.1 to 4.2.4 with material balances and product compositions. Figures 4.2.1 and 4.2.2 show aromatic conversion vs temperature for each of the LCO samples. Figures 4.2.3 to 4.2.6 are bar charts of the mass spectroscopy results for each pressure and LCO sample combination.

The results of the pilot plant work indicate that aromatic saturation improves with increasing temperature and pressure. The increase in aromatic conversion caused a proportional effect on cetane number (Figure 4.2.7). The extent of cracking was not substantial up to temperatures near 380°C. However, judging by the increase in paraffin content, it appears that some alkyl side chains were split off alkylbenzenes. However, the initial boiling points for most of the reaction products were within diesel blending component boiling range.

Although these pilot plant runs have not clearly defined an optimum for aromatic saturation, good results were obtained in the parallel EMR-Gulf study entitled "Improved Synthetic Crude Processing" (6). In this study it was found that the extent of aromatic saturation reaches a maximum in the 380 - 390°C temperature range. The reason for this is an apparent equilibrium effect, beyond which point aromatic saturation declines with increasing temperature. Beyond 390°C, the hydrocracking activity was found to be prevalent with more middle distillate was being lost to the naphtha fraction. The results of the runs in this project also indicate these phenomena, but did not as clearly demonstrate the optimum in aromatic conversion. The information from the parallel project confirmed that, from a aromatic conversion/yield perspective, 380°C was the preferred operating temperature for the production runs. Four production runs were performed in the pilot plant to provide sufficient quantity for the blending study of task #3. The runs were performed at 380°C, 0.8 LHSV for each LCO sample at 15 and 20 MPa pressure.

The production run products confirmed the predictions of the screening runs. The LCO products from 15 and 20 MPa pressure treatment runs had cetane indices (CGSB) of 37.6 and 43.1 respectively. The maxLCO products were only marginally lower in cetane index at 37.3 and 40.5. The mass spectroscopy results as plotted in figures 4.2.3 to 4.2.6 show that less aromatics exist in the maxLCO products then the LCO ones. The cetane contribution of lower boiling cycloparaffins (as evidenced by the lower initial boiling points of maxLCO and mass spec data) is less than that of higher boiling range material. This is congruent with the trend discussed in regard of LSRD/HSRD where the lower cetane exists in the lower boiling range. Overall, it can be seen that the high pressure upgrading of LCOs can be performed effectively to raise ignition quality from less than measurable to the mid-30's where their impact on middle distillate pool quality is likely to be minimal. The effect of raising operating pressure from 15 to 20 MPa has the effect of further improving aromatic conversion from 58% to 82%. The conversion level observed at 10 MPa (lower temperature however) of 0%. The gain in product quality from increasing processing severity has to be weighed against the higher capital and operating costs incurred.

At the end of this effort in this task, the production run samples from the maxLCO runs at 15 and 20MPa were inadvertently mixed together creating a combined product labelled 15/20MPa. Analysis of this product is shown in table 4.2.5. The subsequent blending work in task #3 was adjusted to accommodate this incident with the consent of the EMR Scientific Authority.

4.3 Task #3 Blending of Winter and Summer Grade Diesels and Product Testing

The blending of diesel fuel for the Canadian climate is amongst the

more complicated in product preparations anywhere in the world. The ambient conditions vary widely day to day, season to season and region to region. Due to the wide ranges of conditions faced in the climate, the refiner needs to blend seasonally to meet consumer requirements. In simplification of the seasonal considerations, this projected outlined three basic fuel types to cover year round product requirements for the Western Canadian region. The three basic types of fuels blended were a summer diesel, a spring/fall diesel and a winter diesel. These fuels are designated by their cloud point.

The cloud point of diesel fuel is the temperature at where wax appears. The marketing season minimum temperature has to be above this wax appearance point in order to avoid low temperature inoperability. The wax forms from normal paraffins typically and block equipment fuel systems temperatures below the fuel's cloud point.

The refiner's ability to match seasonal demands for cloud point changes is generally meet by product blending. Each blending component available in the refinery is evaluated for cetane, cloud point and viscosity. Seasonal changes are meet by the proportioning of the blending components according to their cloud point and other properties. Of the three blends, the winter fuel presents the greatist restriction on blending components due to its low cloud point requirements. The blends are further constrained by CGSB specifications (Table 4.3.1) and by the extent of refinery production (shown in Figure 4.3.1). The summer fuel allows more high cloud point blending components to be used (like HSRD) whereas the winter cloud point requirements exclude the use of any high cloud material (western region often can not utilize HSRD in mid-winter). As one would expect, the shoulder seasons, spring and fall, compromise use of high cloud material to the limit of the ambient temperature lows. For this study, the blend cloud points

were chosen as 0°C for summer, -18°C for spring/fall and -40°C for winter.

Blend Formulation

The blending design is discussed along with each blending scenario reported below. The blend formulation for these designs involved a triangular co-ordinate graphing technique, which required;

Step 1 Using the analytical data obtained for the individual blending components, preliminary ternary diagrams were made for each design. Estimates of blend compositions for the limiting blend criteria were plotted as constants or tie-lines.

Step 2: The blend design parameters were located on the preliminary diagram and the blend compositions were estimated. Trial blends were then made to bracket the estimated compositions then tested.

Step 3: The results of the 1st round trial blends were plotted on the preliminary diagram and property tie-lines were redrawn. Further trial blends were generated to fill in data voids and to complete a final ternary blending diagram.

Step 4: A final blends were made based on the completed diagram for each design and these were fully characterized.

The ternary diagrams for all the blend designs are given in Figures 4.3.2 to 4.3.8.

Diesel Fuel Tests

With regards to the CGSB specifications, the list of properties regulated are fuel quality parameters important to the end user. It

is of interest to review the significance of each of these parameters.

Cloud/Pour Point: (ASTM D2500/97)	These properties are the measure of wax crystalization and gelling temperatures which affect the low temperature operability of engines in terms of fuel flow and filter system plugging. These dictate the marketing season for given fuel blends.
Viscosity: (ASTM D445)	Viscosity is one of the most important physical properties of a diesel and significantly affects fuel atomization and influences the lubrication and wear of injection systems
Density/Gravity: (ASTM D1298)	The diesel fuel density has impact on the heating value or energy content and is useful in the calculating fuel quality indices.
Distillation: (ASTM D86)	The boiling range of a diesel fuel can influence the exhaust smoke and odor, engine power and economy, and engine cleanliness.
Water & Sediment: (ASTM D1796)	These limits are obvious for reasons of mechanical wear and potential for creating damage. The combustion of fuel can also be affected.
Sulphur Content: (ASTM D4294)	High amounts of sulphur can affect cylinder and ring wear and accelerate engine deposits. The sulphur in exhaust is also of concern.
Carbon Residue: (ASTM D524)	A measure of residue in the last 10 vol% of distillation range which is proportional to the level of depositional compounds in the diesel.
Cetane No.: (ASTM D613)	The cetane of a fuel is a measure of its ability to ignite in a diesel engine and specifically of ignition delay between ignition and actual combustion. This property affects cold starting, misfiring, noise, smoke, fuel economy and exhaust emissions.

Fuel Stability: (ASTM D2274) — A measurement is made of a fuel's tendency to form precipitates which affects injector sticking, pump deposits, filter plugging, and deterioration in storage.

Scenario 1: Blending and Testing of Current Diesel Product

The desulphurization pilot run products of task #1b were blended with the IPL straight run distillates to formulate the three types of fuels described above. The purpose of doing this was to define the limitations of current blending practise and to evaluate the size of the current middle distillate pool size before alternatives. Using the ternary blending diagram technique the following blending design was executed;

Component	0°C	-18°C	-40°C
LSRD	X	X	X
HSRD	X	X	
LCO	X	X	X
MaxLCO	X	X	X
	6	4	2

The LCO samples used this study were the products of the 10 MPa hydrodesulphurization runs. Their properties are listed in Table 4.3.2 where properties of LSRD are also given. The blending components were combined in trial blends to generate the ternary blending diagrams in Figures 4.3.4 and 4.3.5. Figure 4.3.4 is for the 10 MPa LCO product blends and 4.3.5 is for the 10 MPa MaxLCO blends. The final blend compositions and characterizations are given in Tables 4.3.3 (10 MPa LCO) and 4.3.4 (10 MPa MLCO).

Winter Diesel

The data shows clearly that the blending limitations are most pronounced for winter formulations @ -40°C cloud point. The blend composition choices can only be those in the corner of the ternary diagrams right of the -40°C cloud line. The blends chosen are described in the tables under blend number's 4714 (LCO) and 4720 (MaxLCO). The cloud point restriction for winter fuel requires that HSRD be excluded from the winter blend. This alters the LCO concentration in the winter diesel upwards according to the production ratio and HSRD exclusion. The LCO samples, by virtue of their aromaticity, have low cloud and pour points and can be blended to high levels in winter diesel typically. However, in the case of these samples, the cloud point is not as low as has been experienced and a blend limitation by cloud point was observed for winter diesel. Blends 4714 and 4720 reflected this compromise.

The middle distillate supply in the winter, based on the IPL crude of this project and the proposed blends, would be 23.6 and 25.1 volume % (on crude) for LCO and MaxLCO respectively. The cloud point restriction leaves HSRD (16.9% on crude) unused and leaves 10 to 15% of the LCO's unused. Unused volumes would typically go to inventory or to reprocessing (FCCU) or to bunker/fuel oil streams that have not got the cloud point restrictions. Fortunately, the winter demand for fuels is lower relative to the rest of the year. The western marketing region does, though, have low cloud point fuel demands beyond that in the rest of Canada owing, in part, to resource industry activities in the northern extremes of the region.

Inventories are blended off as ambient conditions dictate. Refiners often build low cloud inventories before the winter season in order to satisfy supply requirements. This involves taking LSRD out of blends when cloud points are not as restrictive. The combustion quality of winter blends does come under pressure because the LSRD has lower cetane and the concentration of LCO becomes more significant when HSRD is excluded from blending.

The low cetane of desulphurized LCO (10 MPa product) degrades the winter blends made here but because the LSRD of this project had a cetane in the 50's, the net affect presents no problem in meeting CGSB requirements. However, if this LSRD had a cetane in the more typical low 40's, the net effect would produce a marginal product which might require additives or exclusion of more LCO than that restricted by cloud point; hence reducing the winter pool size further. All other CGSB requirements are meet quite well by these LCO blends, except the viscosity which passes but is low. The viscosity is important from the lubricity stand point and long term use of the product might accelerate injection system wear. This is not, however, a barrier to the sale of these fuels.

Spring/Fall Diesel Blends

The -18°C cloud point line on the ternary diagrams shows that far more flexibilty in blending spring/fall diesel exists when compared to the winter case. The inclusion of HSRD becomes possible up to the 25 vol% point. Two blends were made to represent spring/fall diesels, a typical inventory situation and a high ratio use of LCO.

The beginning of the spring season usually has the refiner in a high inventory position on HSRD and storage costs dictate that as much HSRD be blended off as the cloud point allows. The LCO supply, meanwhile, is usually short because of the winter's low cloud material demand and is available to the extent that it is produced. Similarly, the LSRD is also available to the extent of production. The blends representing this situation are fuels no.'s 4715 (LCO) and 4721 (MaxLCO). The quality of these blends are good by virtue of the higher density, viscosity, and cetane contributed by the HSRD (cetane no.=61). It should be noted that the blend compositions given in the data tables are from the actual fuels that were tested which incorporate some safety margins on cloud point. The pool size for the spring/fall situation is calculated by adding the production availibility of LCO and LSRD then adding HSRD until the -18°C cloud point limit is reached. The limit of HSRD is 23.8 and 25 vol% for the LCO and MaxLCO blends, respectively. The pool sizes are therefore 31.9 and 34.0 vol% on crude.

The second pair of blends, 4716 (LCO) and 4722 (MaxLCO) are high ratio LCO blends which illustrate the depression affect of low cetane blending components. These fuels have marginal cetanes, relative to the rest and the contribution of the LCOs to the cetane no. is actually lower than their clear cetane factored by volume %. This is to say that LCOs generally blend non-linearly and often shrink in cetane. The SR distillate quality, unfortunately, masks out the impact of these desulphurized examples of LCO and as such, these LCOs can be blended to levels even higher than their production levels. Projecting to the longer term would suggest deterioration of the SR distillate quality and inclusion of LCO may become cetane limited. However, further grace is available from cetane improvers as discussed in scenario 2.

Summer Diesel Blends

The summer season virtually eliminates the blending restrictions the cloud point considerations and at the same time the volume of product sold increases. This enables the refiner to use the HSRD inventory carried from the colder seasons to supplement fuel supply. With the HSRD of this project and the summer cloud point of 0°C, blends of up to 95% HSRD are possible. The blends chosen for the summer fuels were a high ratio HSRD (early & late summer) blend, balanced production (mid-summer) blend and a high ratio LCO blend to observe cetane depression.

The high ratio HSRD blend occurs in early summer as HSRD is used up to reduce winter inventory and it occurs in late summer as LSRD is put into inventory to supply the winter fuel needs. The blends representing this situation are 4717 (LCO) and 4723 (MaxLCO). The cetane quality of these fuels are high owing to the contribution of the HSRD. The token amount of LCO in these has minimal affect on the fuel quantity. The high ratio HSRD blends are usually made over short periods of time because most refiners prefer not to carry to much inventory and can clear or build inventory quickly. The

only impact of the blending criteria on this blend was the level LCO as fixed by production ratio.

The high ratio LCO blends 4719 (LCO) and 4725 (MaxLCO) show the negative affect on cetane that LCOs generally have. Even at these marginal cetane levels, cetane improving additive may be considered to ensure good operability. The high ratio LCO blends, however, don't generally occur unless there has been a production imbalance, like the purchase of a gas oil tender and an extended run of the FCCU.

The balanced production situation of the summer marketing season represents a large proportion of the yearly production and as such is the time when middle distillate supply uses all components to the limit of their production. The blends 4718 (LCO) and 4724 (MaxLCO) were made as the balanced production fuels which emphasizes the production ratio criteria. CGSB specifications and cloud point criteria pose no limitation to these fuels as can be seen in the ternary diagram and the analyses. The middle distillate pool size can be evaluated from these formulations and the ultimate yield can be establish for this scenario. The combined volumes of HSRD and LSRD total to 37.5 vol% of the IPL crude and the average FCCU case raise this to 41 vol%. The quality of fuel was not limited by inclusion of the LCO at all and because of the high SR distillate cetane, LCO could be raised to 35 vol % before reaching the CGSB cetane limit. The maximum LCO FCCU case also does not present any cetane quality problems to the limit of the LCO production ratio and the corresponding pool size is 42 vol% of the crude charged to the refinery. In summary, the fuels blended by season altered the middle distillate pool size according to the cloud point requirements. These seasonal cloud point changed the relative proportion of LCO in the fuels by virtue of exclusion or inclusion of high cloud blending components. In all instances, however, the fuels blended and tested past all CGSB specifications

and cetane quality did not limit the blending level of LCO. The cetane of the straight run distillates were higher than expected and consequently largely masked out the affects of low cetane LCO. The following shows the production levels and fuel quality (assessed as diesel fuel cetane) observed season by season;

	LCO		MaxLCO	
	Production v% on crude	Cetane No.	Production v% on crude	Cetane No.
Winter	23.7	45.4	25.1	41
Spring/Fall	31.9	46.7	34.0	42.1
Summer	41.2	50.1	42.4	44.5

Note: Above yields are based on seasonal blend considerations and the interpolation of Figures 4.3.4 and 4.3.5

Scenario 2: Worst Case LCO Blends and the Use of Ignition Improvers

As can be seen in the data and discussions of scenario 1, the worst case for LCO blending occurs in the winter marketing season where LCO concentration becomes proportionally higher, thus reducing cetane quality. However, even this worst case approach did not lower the cetane to the point where ignition improvers are typically applied. Therefore, the level of LCO blending was raised beyond the level associated with the production criteria in order to evaluate the additive performance in a realistic context. The justification for this was that susceptability studies are only useful for specific ranges of cetane, principally at the CGSB specification minimum. High concentrations of LCO were used basically because the SR distillates had cetane number much higher then expected.

The desulphurization products from the 4.5 and 10 MPa treatment runs were blended in high ratio with LSRD to produce blends with cetane numbers below 40. These fuels were fully characterized and

the analyses are given in Table 4.3.5. The data also includes the cetane numbers measured on these samples with three levels of Diesel Ignition Improver (DII) added. The purpose for varying DII was to demonstrate the cetane number response of low ignition quality LCO blends to state of the art additives. The additive used was an Ethyl product marketed as "Ethyl DII-3" which is an octyl nitrate.

The properties and characteristics are given in Table 4.3.6 which is an Ethyl product bulletin. The cetane number response is plotted in Figures 4.3.9 and 4.3.10 for the 4.5MPa LCOs and 10 MPA LCOs respectively.

The blends manufactured for this scenario, wave the production ratio criteria used in all of the other blending designs, in order to depress the cetane into the range normally treated. The range of concentrations used in these blends covered the expected additive range, of which 0.15 wt% was considered an economic limit. The chemical costs at the 0.15 wt% would cost between 0.3 and 0.5 cents per litre of fuel. The additives have the suspected drawback of increasing the residue (Ramsbottom Carbon Residue, ASTM D524) in the fuels they are used in. Therefore the 10% RCR bottoms were measured on the blends at the maximum treat levels. It can be seen in the data (table 4.3.5) that the DII doesn't consistently increase the RCR content, but the test procedure probably needs updating for sensitivity.

The Ethyl Corporation bulletin (table 4.3.6) gives typical cetane responses for their product. This data has been plotted on the cetane response curves for reference. The Ethyl data, however, was consistently higher than the measured response of the LCOs. This suggests that cycle stocks may not be as susceptable to DII as were other more conventional diesels. The other important observation in this was that the cetane improvement decreases at each increment of

additive; reflecting diminishing returns. Hence, a larger cetane shortfall would cost disproportionately more to achieve the desired product cetane. Overall, DII's are often used as short term solutions to spot situations where blends have not satisfied the specifications. The DII additive does the cetane improvement but the increase in residue is of concern, particularly in the case of blends with LCO in them. The light cycle oils, by themselves, have high residues by virtue of the cracking process they were manufactured in. The LCO's have aromatic and olefin contents which are known to be coke precursors. The refiner will probably avoid this cetane option for the for reasons of cost and potential residue levels and if a long term cetane shortfall was reached, processing would be the perferred route.

Scenario 3: The Improvement of Cetane by LCO Upgrading

The task #2 portion of this project evaluated the Upgrading of LCOs as an alternate means of improving the middle distillate pool cetane. The treatment runs produced four optimized LCO products of which two were inadvertently mix. The blend design in this part of the project had to be modified for the change. The new design was;

Component	0°C	-18°C	-40°C
LSRD	X	X	X
HSRD	X	X	
LCO(15MPa)	X	X	X
MLCO(20MPa)	X	X	X
LCO/MLCO (15/20MPa)	X	X	X
Total Blends	3	3	3

These blends were executed and the ternary diagrams of Figures

4.3.6, 4.3.7 and 4.3.8 were generated. The data on the blends are given in Tables 4.3.7 and 4.3.8.

In the blends formulated based on the upgraded LCOs, only one blend for each season was made. Consequently, the criterias of cloud point, CGSB specifications and production ratios were adhered to.

In review of the blending results, it can be seen that all final products have high cetane values owing to the cetane available from all components in the blends. Again, the fuel with the lowest cetane was the winter diesel which reflects the exclusion of high cetane HSRD. The straight run distillates, as mentioned previously, had cetanes high enough to carry all the LCOs (as produced) to the limit of their production availability. The further quality gained in upgrading the LCOs for blending with these SR distillates was superfluous. The blend cetanes were all in the high 40's. The other fuel qualities were also more than adequate to satisfy CGSB specifications. It can only be conjectured here that, in the case of lower cetane straight run distillates, the need for LCO upgrading would be more significant. As it stands, the middle distillate pool size was not affected but the quality improved;

	LCO			MaxLCO	
	Production v% on crude	Cetane No. (15MPa)	(20MPa)	Production v% on crude	Cetane No.
Winter	23.7	45.1	46.4	25.1	43.0
Spring/Fall	31.9	47.0	47.6	34.0	47.8
Summer	41.2	47.9	48.6	42.4	49.0

Note: Above yields are based on seasonal blend considerations and the interpolation of Figures 4.3.6, 4.3.7 and 4.3.8

Task #4: Reprocessing HCCG for Use in Diesel or Jet Fuel

The work conducted in this task was in two parts; the first part being the original work statement items and the second being the work of the ammended progam. In the first part, the originally scoped two stage treatment of HCCG was performed and along with some preliminary trials on one stage treatment. Calculations were performed on one stage treatment and the feasibility of single stage processing was determined, for which a a program ammendment was drafted and accepted.The single stage treatment option was optimized for space velocity (LHSV), a critical processing cost factor, and a production was performed to generate product for evaluation.

The work progressed in the following manner;

Part 1: Two Stage HCCG Processing

The pilot plant work included;

- obtaining and running HCCG (ex Clarkson) to screen run conditions (Clarkson feed was used to supplement the work due to Edmonton feed limitations)
- 2 stage hydrotreating of Edmonton HCCG
- single stage hydrotreating of Edmonton HCCG at 1 and 2 LHSV
- treatment product evaluation

The catalyst used in these runs was Katalco NM506 based on the outcome of a parallel Gulf/EMR project* which screened middle distillate treating catalysts for performance.

The hydrotreatment of the HCCG feed was expected to be strongly exothermic by virtue of the olefins and aromatics present. The two stage rationale was to mildly treat the HCCG to convert olefins to saturates in the first pass and to convert aromatics to naphthenes in a more severe second pass. The pressures were assigned by the work statement as 4.1 and 10.3 MPa respectively. However, the other

run conditions (LHSV,Temp.) were not known and a screening excercise was required to set production run parameters.

A HCCG feed similar to the (Gulf) Edmonton HCCG was obtained from the (Gulf) Clarkson FCCU and was used to determine a suitable operating temperature (Analyses in Table 4.1.2). The LHSV chosen was based on the limitations of feed and reactor size. This dictated that the maximum practical LHSV was 2 in order to allow realistic lineout times and provide sufficient quantities of products from the limited feed (approx. 80 litres of feed). The temperature was varied between 250 and 350°C for both first and second stages to map out the olefinic and aromatic conversions. Figures 4.4.1 and 4.4.2 show the effect of reactor temperature on product aromatics and bromine number. It can be seen that the first stage treatment (4.1 MPa) converts all the olefins at or near 300°C. The aromatics at the same conditions are minimally affected. The second stage treastment (10.3 MPa) showed that aromatics steadily declined over the range of temperature and in the parallel Gulf/EMR project (6) it was observed that a maximum conversion would be achieved at 385°C using Katalco NM506 (catalyst properties given Table 4.4.1). The production run operating conditions were then set as;

- 2 LHSV, 4.1 MPa, 300°C for the 1st stage
- 2 LHSV, 10.3 MPa, 385°C for the 2nd stage
- 1 & 2 LHSV, 10.3 MPag, 385°C for the one step processing evaluation

The run results for Edmonton HCCG are given in Table 4.4.2 and include mass spectrometry, distillation cloud point, pour point and smoke point data. Two gallons of each product was collected. The results showed that:

- all products have exceptionally low cloud and pour points and exhibit good smoke points
- two stage processing at 2 LHSV achieves only slightly better aromatic conversion compared to single stage (67% vs 65%)

- single stage treatment at 1 LHSV achieved 88% conversion of aromatics but produced 50 vol% of product outside the original boiling range, compared to 67% aromatic conversion and 30 vol% of product outside the original B.P. range for 2 stage (@ 2 LHSV)
- an intermediate LHSV, between 1 and 2, may have optimized yield vs conversion
- the feasibility of one stage treatment would only depend on whether the net heat of reaction in a adiabatic catalyst bed would be controllable by reactant mass flow and hydrogen quench; the P-12 reactor is too small to assess this and heat balancing calculations had to be performed to address feasibility

The feasibility of single stage processing of HCCG in a commercial reactor, at the pressure, temperature, and space velocity used in this study, was reviewed. A typical commercial reactor would be able to handle the HCCG treatment if provision is made for the mid-catalyst bed H_2 quenching. Figure 4.4.3 shows a schematic of a typical hydrotreater and illustrates the basis of the following heat balance.

Using the collected mass spectrometry data for the pilot plant runs (Table 4.4.2) one can perform an estimate on the reactor heat balance. Data from run 2047 were selected as this run represents the most severe operation envisaged for treating the HCCG. The reactions that take place in the catalyst bed were assumed to be

(a) Olefin Saturation
(b) Desulphurization/Denitrogenation
(c) Aromatic Saturation

The heat of reaction was then estimated for representative molecular changes in each of these groups. The conditions of run 2047 (ie pressure and temperature) are such that all reactions take place in the liquid phase and there is no phase change to be accounted for. On the basis of 1 m^3 of HCCG feed to the reactor, the following was estimated;

(a) Olefin Saturation

The Bromine No. of Edmonton HCCG was found to be 10.5 which is approximately 5.4 wt% olefins with an average molecular weight of 96. To calculate the heat released by hydrogenation, the conversion of a C_7 alkene to a C_7 alkane was used.

C_7 Alkene + H_2 <-> C_7 Alkane @ 100% conversion
H_f = -75.31 kJ/gmole <-> -188.28 kJ/gmole
H_r = -112.97 kJ/gmole

In 1 m^3 of HCCG, approximately 460.5 gmole of C_7 alkene was present and the heat generated in saturating was roughly 52 MJ/m^3 HCCG.

(b) Desulphurization/Denitrogenation

The HCCG contained approximately 1500 wppm combined N_2 and S_2 compounds. Using a desulphurization reaction to represent the molecular change for this group;

Methylthiophene + H_2 <-> H_2S + Methylbutane
H_f = -83.85 kJ/gmole <-> -20.17 + - 153.97 kJ/gmole
H_r = -90.29 kJ/gmole

In 1 m^3 of HCCG, 38.58 gmole of sulphur (expressed as methyl thiophene) was present and the heat generated by this type of reaction would be 3.5 MJ/m^3 HCCG.

(c) Aromatic Saturation

The bulk of the reaction heat was generated by the conversion of aromatics to cycloparaffins because this reaction was the one being maximized in the processing runs. Based on the mass spectroscopy data for the feed and product from run 2047, a balance can be

performed on aromatics. From Table 4.4.2 it can be seen that there were essentially only C_8 and C_9 to contend with.

[C_8]: The assumed C_8 aromatic reaction was xylene to dimethylcyclohexane

xylene + nH_2 <-> dimethylcyclohexane

H_f = +19.08 kJ/gmole <-> -172.09 kJ/gmole

H_r = -191.17 kJ/gmole or 370 MJ/m^3 HCCG (based on net xylene make)

[C_9]: The assumed C_9 aromatic reaction was propylbenzene to propylcyclohexane

iso/n-propylbenzene + nH_2 <-> iso/n-propylcyclohexane

H_f = +5.96 kJ/gmole <-> -193.18 kJ/gmole

H_r = -199.14 kJ/gmole or 363 MJ/m^3 HCCG (based on net alkylbenzene content)

The overall heat of reaction estimate for one stage hydrotreating at 10.3 MPa, 385°C, and 1 LHSV was 789.0 MJ/m^3 HCCG feed. This heat is exothermic and represents the heat to be dissipated by heat loss and/or quenching in order to maintain stable operation.

Feasibility of One Stage Hydrotreating HCCG

A commercial scale reactor would behave almost adiabatically and the heat generated by exothermic reactions would have to be removed in order to maintain a given operating temperature. Two possible mechanisms are;

(a) Reducing HCCG preheat such that the reactor inlet feed temperature is less than the reaction average temperature.
(b) Hydrogen quenching at points along the length of the reaction bed.

These reaction control strategies can be applied to the proposed single stage operation on HCCG as to offset the exothermic heat of reaction. Applying strategy (a) would reduce system heat by 144 MJ/m^3 if the feed entered the reactor at 340°C. Applying strategy (b) would reduce system heat by 645.5 MJ/m^3 if the quench rate was 1500 m^3/m^3 hydrogen (at T_i = 38 °C). The heat of reaction is balanced by the above examples and supports the feasibility of one stage processing.

Work Statement Amendment

In light of the foregoing assessment and the importance of HCCG utilization for future distillate fuel needs; it was proposed that Task # 4 be amended to include pilot plant optimization runs. These optimization runs were needed to identify the reaction space velocity which would maximize middle distillate blending component yield and satisfy the CGSB cumbustion quality requirements.

The work included;

(1) Four pilot plant screening runs @ 1, 1.5, 2, and 2.5 LHSV (10.3 MPa/385°C).
(2) Screening run product evaluation for cetane no. and smoke point
(3) Pilot plant production run at the optimum LHSV to produce fuel for evaluation.
(4) Product evaluation for use as jet fuel or as ablending component in diesel fuel.

The work involved characterization of both intermediate and production run products as per the original plan. However, it was necessary to obtain further HCCG feedstock to perform the revised program and the analysis of this feed is given along with the other HCCG samples in Table 4.1.2.

Part 2: Optimization of Single Stage HCCG Reprocessing

The pressure condition for the pilot plant runs remained at 10.3 MPa which was originally chosen to relate to modern distillate treaters (unit pressures higher than 10.3 MPa are not common). The operating temperature was also kept at the temperature found to be an optimum for aromatic conversion to naphthenes, namely 385°C. The remaining process variable to be assessed was space velocity, a direct link to processing cost. The objective of the LHSV screening runs performed was to map a range of aromatic conversion from which an optimum space velocity could be interpolated. The optimum was determined by maximum unit throughput and CGSB specs. criteria. The screening runs at each of 1, 1.5, 2, and 2.5 LHSV produced products which were analyzed for composition. Data on these is given in Table 4.4.3. Figure 4.4.4 shows the effect of LHSV on product smoke point. Figure 4.4.5 shows the effect of LHSV on product aromatics and cetane no. As can be seen by these figures, the effect of LHSV was major over the range tested, especially with regards to product aromatic content. The review of the collected data indicated an opportunity of making jet fuel (type B) directly due to the boiling range of HCCG and the achievable smoke point. The cetane number achieved in the products of the screening runs were below the diesel specification and would be another LCO type blending component. The Jet B option for these products is desirable because further blending or processing (eg distillation) is not required and this stream could be segregated directly (after the hydrotreater) from other refinery streams and accessed as required. With this in mind the production run was tuned for 22 mm smoke point. This production target was chosen to provide a safety margin above the CGSB specification minimum.

Interpolation of Figure 4.4.4, indicates that a LHSV of 1.9 corresponds to a 22 mm smoke point product. This LHSV and 385°C and 10.3 MPa were used as the production run conditions. The data on this run is also included in Table 4.4.3.

The final product was evaluated as a stand alone jet fuel as well as for a diesel blending component. The results of the product testing are contained in Table 4.4.4. It can be seen that reprocessed HCCG can make satisfactory Jet B under existing CGSB specifications and at the HCCG production level found in this project can also be blended into the middle distillate pool with negligible impact on diesel cetane number. The cloud and pour point characteristics of reprocessed HCCG allows its inclusion in any of the fuels blended earlier. Revising the earlier middle distillate pool size estimates (Maximum LCO case only due to this HCCG boiling point range);

	MaxLCO (10 MPa)		MaxLCO (15/20 MPa)	
	Production v% on crude	Cetane No.	Production v% on crude	Cetane No.
Winter	26.7	40.2	26.7	42.1
Spring/Fall	35.6	41.5	35.6	46.9
Summer	44.0	43.9	44.0	48.2

5.0 CONCLUSIONS

The earlier discussion has dealt with the measured results and their interpretation. At the end of the work in this project the following conclusions were drawn:

5.1 The LCO from typical FCCU operations can be significantly upgraded from <20 to near 40 Cetane Number by hydroprocessing with commercial catalyst. The reaction optimized in this work was aromatic saturation and this was favoured by low LHSV, high pressure and temperature up to 385°C.

5.2 The cetane numbers of the straight run distillates obtained from the IPL crude sample taken for this project were higher than expected and allowed full utilization of traditional LCO to limit of production.

5.3 The fuel blend modelled in this work that came under the most ignition quality pressure was the winter blend. This is observed commercially and was reproduced in this study. The cloud point constraint on winter diesel excluded the use of high cetane heavy straight run distillate. Consequently the usable yield of middle distillate was dramatically reduced relative to yields for other seasons. The low cloud point availability becomes a key concern for winter fuel formulation and the use of LCO significantly supplemented the winter fuel blending. The cetane of LCO had the strongest influence in this blend and would not have met the CGSB specification had the light straight run distillate been lower than 46 in cetane number.

5.4 The high pressure upgraded LCO products reduced the need for high cetane in the straight run distillates and the winter blends in particular would have tolerated a light straight run distillate with a cetane number under 42 to make a 40 CN blend.

5.5 The use of cetane improver was investigated for high ratio LCO blends and it was determined that a 38 CN blend could be corrected with a .03 to .05 wt% treatment with a leading commercial additive. However, this approach to cetane improvement was not considered a viable long term solution to ignition quality requirements in diesel fuel.

5.6 The reprocessing of HCCG by hydrogenation was investigated in detail and it was found that single stage processing was possible if adequate quench and reactor preheater allowances were made. The objective in HCCG hydrogenation was the saturation of aromatics to improve ignition quality. It was found that a LHSV of 1.9 and an operating temperature of 385°C at 10.3 MPa pressure produced a satisfactory Jet B product from HCCG.

6.0 RECOMMENDATIONS

In light of the foregoing results and discussions, we recommend:

6.1 An investigation of FCCU operation changes to increase the yield of LCO should be undertaken. The winter diesel fuel cloud point constraint and resultant low crude yield could be enhanced by upgraded LCO from an expanded LCO FCCU operation.

6.2 An evaluation of the Heavy Cycle Oil as a feed for a hydrocracking should be carried out. The hydrocracking of HCO may provide more low cloud point and high energy content blending component for the middle distillate pool.

6.3 Distillates from residuum upgrading operations should be studied as fuel blending components. For example, coker distillates are common in refineries and possess aromatic qualities degrading the middle distillate pool. A hydroprocessing study of these types of components would investigate further expansion of the middle distillate from the bottom of the barrel of crude.

6.4 A cetane number survey of straight run distillates from Canadian crude sources and a study of relative production levels should be performed to track the ignition quality of the middle distillate aggregate over time.

6.5 A production run should be made to produce upgraded LCO for the study of commercial engine operation on high ratio blends of LCO and straight run distillate. This would evaluate the depositional tendancies and combustion stability of these high ratio LCO blends in commercial combustion equipment.

6.6 Reprocessed HCCG as Jet B should be evaluated in a test engine to determine its effect on conventional turbine combustion. The reprocessing of HCCG is an important approach to Jet B production owing to its logistical simplicity.

REFERENCES

1. Emmett, Paul H.,(Editor) Catalysis 1957, Reinhold Publishing

2. Lieberman, Norman P., "Troubleshooting Refinery Processes",1981, PennWell Publishing Company

3. Hengstebeck, R.J., "Petroleum Processing", 1959, McGraw Hill

4. "Engines, Fuels and Lubricants- A Perspective on the Future", 1980, Published by SAE

5. Gruse, William A., " Motor Fuels, Performance and Testing", 1967, Reinhold Publishing

6. Deutscher, R.R., Simmons, R.A., Final Report " Development of Synthetic Crude Processes and Their Impact on Distillate and other Product Qualities", Canmet Project Number 23440-3-9057

TABLE 4.1.1: Properties of LSRD and HSRD

		Light Straight Run Distillate (LSRD)	Heavy Straight Run Distillate (HSRD)
Cut Range (TBP) °C		165 - 270	270 - 370
Position in Crude, Vol%	from	29.09	49.69
	to	49.69	66.62
Yield, Vol% on Crude		20.60	16.93
Density, @15°C		0.8141	0.8588
°API Gravity	D1298	42.2	33.2
Flash Point, °C	D93	60	130
Cloud Point, °C	D2500	-48	+2
Pour Point, °C	D97	-48	-3
Smoke Point, mm	D1322	24.0	15.7
Aniline Point, °C	D611	59.5	75.8
Viscosity, cSt @40°C	D455	1.5	5.4
Sulphur, wt%	D1266	0.1	0.5
Nitrogen, wppm	D3431	<1	175
Cetane No.	D613	48	61
Distillation, °C	D86		
IBP		180	288
10%		193	299
30%		204	302
50%		216	308
70%		231	319
90%		247	335
FBP		261	347
Composition, M.S. wt%			
Paraffins		44.4	29.9
Cycloparaffins		38.5	47.8
Monoaromatics		14.6	12.3
Diaromatics		2.5	7.4
Triaromatics		0.0	1.3
Tetraaromatics		0.0	0.3
Pentaaromatics		0.0	0.0

TABLE 4.1.2 Comparison of HCCG Samples

Sample > / Property		Edm HCCG D83-118	Clkn HCCG (Screening)	Clkn HCCG CKM 456B
Density @ 15°C		0.8247	0.8170	0.8156
Bromine No.		9.35	22.11	22.30
Distillation D86, °C	IBP	145	141	131
	10%	148	144	143
	30%	150	148	147
	50%	152	151	151
	70%	155	156	156
	90%	161	165	166
	FBP	189	197	181
Mass Spectroscopy Compositional, Vol%				
	Paraffins	23.6		23.9
	Olefins	--		15.3
	Naphthenes	19.0		18.7
	Aromatics	57.4		42.1

TABLE 4.1.3: Properties of LCO and MaxLCO

		Light Cycle Oil (LCO)	Maximum Light Cycle Oil (MLCO)
FCCU Product Cut Range (TBP) °C		200 - 340	170 - 340
Yield, Vol% on Crude*		3.7	4.9
Density, @15°C		0.9504	0.9289
°API Gravity	D1298	16.8	20.5
Flash Point, °C	D93	85	66
Cloud Point, °C	D2500	--	-19
Pour Point, °C	D97	-21	-30
Viscosity, cSt @40°C	D455	2.85	2.08
Sulphur, wt%	D1266	1.00	0.82
Cetane No.	D613	<21	<21
Cetane Index		23.8	23.3
Distillation, °C	D86		
IBP		202	176
10%		236	201
30%		257	224
50%		278	255
70%		305	291
90%		340	335
FBP		357	350
Composition, M.S. wt%			
Paraffins		11.5	13.6
Cycloparaffins		7.7	9.3
Monoaromatics		21.8	36.3
Diaromatics		45.6	32.4
Triaromatics		9.4	5.9
Tetraaromatics		0.4	0.2
Pentaaromatics		0.0	0.0
Aromatic Sulphur		3.6	2.3

Table 4.1.4: Properties of Katalco NT550 Catalyst

KATALCO NT 550 nickel-tungsten hydrotreating catalyst shows superior desulfurization, denitrogenation, and aromatics saturation activity at elevated pressures. It also exhibits excellent selectivity in many hydrogenation reactions.

TYPICAL CHEMICAL ANALYSIS, WT. %, DRY BASIS

WO_3	20.0%
NiO	5.0%
Alumina Base	Balance

TYPICAL PHYSICAL PROPERTIES

Form	Extrudate	
Size	1/10" (Nom 1/8")	1/16"
Surface Area, sq m/gm	230	230
Total Pore Volume, ml/gm	0.50	0.50
Density (Vibrated), gm/ml	0.79 – 0.81	0.79 – 0.81
Reactor Packed Density, lb/cu ft	45 – 47	45 – 47
Strength, lb Crush	16 – 18	14 – 16
Attrition Index*	97	97

*% retained on a 20-mesh sieve after tumbling for one-half hour

HANDLING

Avoid eye and skin contact. Do not take internally.

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TABLE 4.1.5: Pilot Plant LCO Desulphurization Runs

	Feed	#7020 LCO	#7009 LCO
Run Conditions			
Temperature, °C		311	325
Pressure, MPa		4.5	10
LHSV, hr^{-1}		0.80	0.80
H_2 Consumption, m^3/m^3		43	164
Product Properties			
Density @ 15°C	0.950	0.940	0.917
Viscosity @ 40°C, cst.	2.9	2.8	2.7
Flash Pt.,°C		72	78
Cloud Pt.,°C		-17	-18
Pour Pt.,°C		-18	-21
Aniline Point		8	11
Sulphur, wt%		0.52	0.08
Distillation, D86 °C			
IBP		186	185
10%		233	229
30%		253	246
50%		272	250
70%		300	286
90%		336	322
FBP		350	340
MS Compositional,wt%			
Saturates			
Paraffins	11.5	12.9	10.2
Cycloparaffins	7.7	7.7	10.9
Aromatics			
Monoaromatics	21.8	41.2	68.5
Diaromatics	45.6	33.0	8.7
Triaromatics	9.4	4.2	1.0
Tetraaromatics	0.4	0.1	0.0
Pentaaromatics	0.0	0.0	0.0
Thiophenes	3.6	1.6	0.8
Cetane No.	<21.0	<21.0	22.8

TABLE 4.1.6: Pilot Plant MaxLCO Desulphurization Runs

Run Conditions	Feed MLCO	#7029 MLCO	#7034 MLCO
Temperature, °C		310	325
Pressure, MPa		4.5	10
LHSV, hr^{-1}		0.80	0.80
H_2 Consumption, m^3/m^3		46	166
Product Properties			
Density @ 15°C	0.929	0.918	0.897
Viscosity @ 40°C, cst.	2.1	2.0	1.9
Flash Pt., °C		47	65
Cloud Pt., °C		-16	-22
Pour Pt., °C		-27	-30
Aniline Point		4	12
Sulphur, wt%		0.34	0.00
Distillation, D86 °C			
IBP		174	172
10%		200	198
30%		222	219
50%		262	242
70%		283	270
90%		328	312
FBP		346	333
MS Compositional, wt%			
Saturates			
Paraffins	13.6	12.6	12.9
Cycloparaffins	9.3	8.1	12.2
Aromatics			
Monoaromatics	36.3	52.4	68.6
Diaromatics	32.4	23.5	5.2
Triaromatics	5.9	3.0	0.7
Tetraaromatics	0.2	0.1	0.0
Pentaaromatics	0.0	0.0	0.0
Thiophenes	2.3	0.4	0.4
Cetane No.	<21.0	<21.0	23.0

TABLE 4.2.1: Pilot Plant LCO Upgrading Runs @ 15 MPa

	Feed	#7041	#7044	#7049	Final
Run Conditions					
Temperature, °C	--	340	360	380	380
Pressure, MPa	--	15	15	15	15
LHSV, hr^{-1}	--	0.80	0.80	0.80	0.80
H_2 Consumption, m^3/m^3	--	216	278	323	375
Product Properties					
Density @ 15°C	0.950	0.905	0.891	0.879	0.875
Viscosity @ 40°C, cst.	2.9	2.5	2.3	2.4	2.6
Flash Pt.,°C			61	54	87
Cloud Pt.,°C					-18
Pour Pt.,°C					-24
Aniline Point		23	33	44	60
Sulphur, wt%		<0.01	<0.01	<0.01	<0.01
Distillation, D86 °C					
IBP		167	153	142	215
10%		216	216	213	229
30%		237	237	233	239
50%		254	252	248	251
70%		275	272	268	271
90%		313	306	303	305
FBP		333	331	331	337
MS Compositional,wt%					
Saturates					
Paraffins	11.5	13.3	13.7	13.1	11.4
Cycloparaffins	7.7	19.6	35.1	49.8	56.3
Aromatics					
Monoaromatics	21.8	60.7	47.5	34.1	29.1
Diaromatics	45.6	5.1	2.3	1.3	1.2
Triaromatics	9.4	1.0	1.4	1.6	1.9
Tetraaromatics	0.4	0.1	0.0	0.0	0.0
Pentaaromatics	0.0	0.0	0.0	0.0	0.0
Thiophenes	3.6	0.4	0.0	0.0	0.0
Cetane No.	<21	24.7	28.5	33.5	35.1

TABLE 4.2.2: Pilot Plant MaxLCO Upgrading Runs @ 15 MPa

Run Conditions	Feed	#7036	#7037	#7038	Final
Temperature, °C	--	340	360	380	380
Pressure, MPa	--	15	15	15	15
LHSV, hr^{-1}	--	0.81	0.80	0.80	0.80
H_2 Consumption, m^3/m^3	--	232	280	329	375
Product Properties					
Density @ 15°C	0.929	0.886	0.878	0.865	0.875
Viscosity @ 40°C, cst.	2.1	1.9	1.9	1.8	1.8
Aniline Point		22	33	43	49
Sulphur, wt%		<0.01	<0.01	<0.01	<0.01
Distillation, D86 °C					
IBP		171	164	156	148
10%		192	196	191	182
30%		212	215	211	
50%		234	234	236	225
70%		263	264	259	
90%		303	304	300	291
FBP		331	329	328	328
MS Compositional, wt%					
Saturates					
Paraffins	13.6	14.0	14.3	13.7	13.1
Cycloparaffins	9.3	23.9	37.3	52.7	62.2
Aromatics					
Monoaromatics	36.8	59.1	46.0	31.4	23.1
Diaromatics	32.4	2.1	1.1	0.8	0.4
Triaromatics	5.9	1.0	1.3	1.4	1.2
Tetraaromatics	0.2	0.0	0.0	0.0	0.3
Pentaaromatics	0.0	0.0	0.0	0.0	0.0
Thiophenes	2.3	0.0	0.0	0.0	0.0
Cetane No.	<21.0	25.0	28.1	31.8	32.6

TABLE 4.2.3: Pilot Plant LCO Upgrading Runs @ 20 MPa

	Feed	#7057	#7058	Final
Run Conditions				
Temperature, °C	--	340	360	380
Pressure, MPa	--	20	20	20
LHSV, hr^{-1}	--	0.80	0.80	0.80
H_2 Consumption, m^3/m^3	--	331	350	427
Product Properties				
Density @ 15°C	0.950	0.884	0.880	0.867
Viscosity @ 40°C, cst.	2.90	2.3	2.4	2.7
Flash Pt., °C		65	49	87
Cloud Pt., °C				-18
Pour Pt., °C				-24
Aniline Point		38	44	60
Sulphur, wt%		<0.01	<0.01	<0.01
Distillation, D86 °C				
IBP		168	154	214
10%		218	214	226
30%		236	235	236
50%		249	249	248
70%		266	269	266
90%		299	305	300
FBP		321	327	335
MS Compositional, wt%				
Saturates				
Paraffins	11.5	14.0	13.3	11.8
Cycloparaffins	7.7	39.9	48.2	74.5
Aromatics				
Monoaromatics	21.8	43.1	35.6	11.0
Diaromatics	45.6	1.6	0.9	0.7
Triaromatics	9.4	1.5	1.8	2.0
Tetraaromatics	0.4	0.0	0.0	0.0
Pentaaromatics	0.0	0.0	0.0	0.0
Thiophenes	3.6	0.0	0.0	0.0
Cetane No.	<21.0	30.1	32.7	36.1

TABLE 4.2.4: Pilot Plant MaxLCO Upgrading Runs @ 20 MPa

Run Conditions	Feed	#7062	#7067	#7065	Final
Temperature, °C	--	362	380	390	382
Pressure, MPa	--	20	20	20	20
LHSV, hr^{-1}	--	0.80	0.80	0.80	0.80
H_2 Consumption, m^3/m^3	--	401	446	441	414
Product Properties					
Density @ 15°C	0.929	0.858	0.844	0.842	0.849
Viscosity @ 40°C, cst.	2.1	2.0	1.9	1.8	2.0
Flash Pt.,°C			43		
Cloud Pt.,°C			-26		
Pour Pt.,°C			-33		
Aniline Point		55	62	60	55
Sulphur, wt%		<0.01	<0.01	<0.01	<0.01
Distillation, D86 °C					
IBP		156	146	129	148
10%		197	186	180	182
30%		217	210	204	
50%		235	229	223	224
70%		256	252	247	
90%		294	290	288	292
FBP		318	319	315	327
MS Compositional,wt%					
Saturates					
Paraffins	13.6	13.0	11.5	11.8	12.5
Cycloparaffins	9.3	69.7	83.5	80.9	74.0
Aromatics					
Monoaromatics	36.3	15.2	3.7	6.1	12.0
Diaromatics	32.4	0.4	0.2	0.2	0.0
Triaromatics	5.9	1.4	1.1	1.1	1.2
Tetraaromatics	0.2	0.0	0.0	0.0	0.0
Pentaaromatics	0.0	0.0	0.0	0.0	0.0
Thiophenes	2.3	0.0	0.0	0.0	0.0
Cetane No.	<21.0	36.3	40.1	37.9	35.3

TABLE 4.2.5: 15/20 MPa MaxLCO Combined Product

	Feed	#7070 & #7073
Run Conditions		
Temperature, °C	--	381
Pressure, MPa	--	15/20
LHSV, hr^{-1}	--	0.80
H_2 Consumption, m^3/m^3	--	430
Product Properties		
Density @ 15°C	0.929	0.856
Viscosity @ 40°C, cst.	2.1	2.0
Flash Pt., °C		
Cloud Pt., °C		-18
Pour Pt., °C		-39
Aniline Point		54
Sulphur, wt%		<0.01
Distillation, D86 °C		
IBP		185
10%		200
30%		213
50%		229
70%		253
90%		292
FBP		329
MS Compositional, wt%		
Saturates		
Paraffins	13.6	11.8
Cycloparaffins	9.3	68.0
Aromatics		
Monoaromatics	36.3	18.3
Diaromatics	32.4	0.5
Triaromatics	5.9	1.4
Tetraaromatics	0.2	0.0
Pentaaromatics	0.0	0.0
Thiophenes	2.3	0.0
Cetane No.	<21.0	36.5

Table 4.3.1: CGSB Diesel Fuel Specifications

		TYPE AA	TYPE A	TYPE B	Method Méthode ASTM
Flash Point Point d'éclair	°C, Min.	40	40	40	D 3828 D 93 (Note 4) (Remarque 4)
Cloud Point Point de trouble	°C, Max.	-48	-34	(Note 5) (Remarque 5)	D 2500
Pour Point Point d'écoulement	°C, Max.	-51	-39	(Note 5) (Remarque 5)	D 97 (Note 6) (Remarque 6)
Kinematic Viscosity at 40°C, mm2/s (cSt) (Note 7) Viscosité cinématique à 40°C, mm2/s (cSt) (Remarque 7)	Min. Max.	1.2 -	1.3 4.1	1.4 4.1	D 445
Distillation: 90% Recovered Récupéré à 90%	°C, Max.	290	315	360	D 86
Water and Sediment, % vol. Eau et sédiment, % en vol.	Max.	0.05	0.05	0.05	D 1796 (Note 8) (Remarque 8)
Total Acid Number Indice d'acide total	Max.	0.10	0.10	0.10	D 974
Sulphur, % mass (Note 9) Soufre, % en masse (Remarque 9)	Max.	0.2	0.5	0.7	D 1552 (Note 10) (Remarque 10)
Copper Corrosion 3 h at 100°C Corrosion du cuivre 3 h à 100°C	Max.	No./No 1	No./No 1	No./No 1	D 130
Carbon Residue (Ramsbottom), on 10% bottoms, % mass (Note 11) Résidue de carbone (Rambsbottom) sur 10% de résidus, % en masse (Remarque 11)	Max.	0.15	0.15	0.20	D 524
Ash, % mass Cendre, % en masse	Max.	0.01	0.01	0.01	D 482
Ignition Quality, Cetane No. (Note 12) Aptitude à l'allumage, indice de cétane (Remarque 12)	Min.	40	40	40	D 613

TABLE 4.3.2A: Blending Component Characterization Data

Component	ASTM Method	LSRD	HSRD	LCO Treatment Products 4.5MPa	10 MPa	15 MPa	20 MPa
°API Gravity		42.2	33.2	19.1	22.8	30.2	31.7
Density	D1298	0.814	0.859	0.940	0.917	0.875	0.867
Flash Pt.,°C	D93	60	130	71.5	78	88	87
Aniline Pt,°C	D611	59.5	75.8	7.6	10.6	50.6	60.0
Cloud Pt.,°C	D2500	-48	+2	-17	-18	-16	-18
Pour Pt.,°C	D97	-48	-3	-18	-21	-24	-24
Viscosity @ 40°C, cst.	D445	1.53	5.36	2.81	2.73	2.62	2.68
Sulphur, wt%	D4294	0.11	0.50	0.52	0.32	0.003	0.003
Residue on 10% Bottoms, wt% clear	D524	0.10	0.04	0.31	0.36	0.05	0.04
Distill'n,°C	D86						
IBP		180	288	186	185	215	214
10%		193	299	233	229	229	226
50%		216	308	272	262	251	248
90%		247	335	336	322	305	300
FBP		261	347	350	340	337	335
% Recovery		99.4	99.0	98.5	99.0	98.0	99.0
Blending Cetane No.	D613	48	61	-2.6	18.9	20.0	33.6

TABLE 4.3.2B: Blending Component Characterization Data

Component	ASTM Method	LSRD	HSRD	MaxLCO Treatment Products 4.5MPa	10 MPa	15/20 MPa
°API Gravity		42.2	33.2	22.7	26.3	33.8
Density	D1298	0.814	0.859	0.918	0.897	0.856
Flash Pt.,°C	D93	60	130	47	65	66
Aniline Pt,°C	D611	59.5	75.8	3.6	12.1	53.6
Cloud Pt.,°C	D2500	-48	+2	-16	-22	-18
Pour Pt.,°C	D97	-48	-3	-27	-30	-39
Viscosity @ 40°C, cst.	D445	1.53	5.36	2.00	1.94	2.00
Sulphur, wt%	D4294	0.11	0.50	0.34	0.08	0.002
Residue on 10% Bottoms, wt% clear	D524	0.10	0.04	0.30	0.10	0.04
Distill'n,°C	D86					
IBP		180	288	174	172	185
10%		193	299	200	198	200
50%		216	308	250	242	229
90%		247	335	328	312	292
FBP		261	347	346	313	329
% Recovery		99.4	99.0	99.0	98.5	98.5
Blending Cetane No.	D613	48	61	-1.4	13.0	36.1

TABLE 4.3.3: 10 MPa LCO Blend Compositon Data

Blend Composition		Winter	Fall/Spring		Summer		
LSRD, vol%		87	66	51	15	49.7	35.4
HSRD, vol%		--	24	17	75	40.3	28.6
LCO, vol%		13	10	32	10	10	36
Blend No.		4714	4715	4716	4717	4718	4719
	ASTM Method						
°API Gravity		39.3	37.9	33.9	33.3	36.5	32.2
Density	D1298	0.828	0.835	0.855	0.858	0.842	0.864
Flash Pt.,°C	D93	64	66	68	89	69	74
Cloud Pt.,°C	D2500	-42	-21	-18	-6	-15	-14
Pour Pt.,°C	D97	-45	-39	-30	-12	-18	-24
Viscosity @ 40°C, cst.	D445	1.56	2.00	2.14	3.92	2.44	2.55
Sulphur, wt%	D4294	0.14	0.23	0.25	0.43	0.29	0.30
Residue on 10% Bottoms, wt% clear	D524				0.30		0.26
Distill'n,°C	D86						
IBP		179	179	184	203	187	187
10%		194	195	202	246	206	212
50%		220	238	245	297	258	249
90%		257	309	315	324	321	321
FBP		300	339	340	344	339	339
% Recovery		98.8	98.5	98.5	99.2	98.7	98.7
Cetane No.	D613	45.4	46.7	43.7	49.5	50.1	43.0

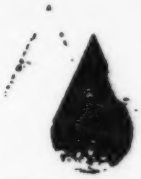
TABLE 4.3.4: 10 MPa MaxLCO Blend Compositon Data

Blend Composition		Winter	Fall/Spring		Summer		
LSRD, vol%		82	58.3	51	9.8	48	39.8
HSRD, vol%		--	25	23	77	38.8	32.2
MaxLCO, vol%		18	16.7	26	13.2	13.2	28
Blend No.		4720	4721	4722	4723	4724	4725
	ASTM Method						
°API Gravity		39.1	37.1	35.7	33.1	36.5	34.7
Density	D1298	0.829	0.839	0.846	0.859	0.842	0.851
Flash Pt.,°C	D93	60	66	67	89	68	63
Cloud Pt.,°C	D2500	-42	-21	-21	-6	-15	-15
Pour Pt.,°C	D97	-45	-39	-33	-9	-24	-24
Viscosity @ 40°C, cst.	D445	1.54	2.70	2.03	3.95	2.33	2.27
Sulphur, wt%	D4294	0.10	0.20	0.19	0.41	0.26	0.23
Residue on 10% Bottoms, wt% clear	D524	0.30					0.09
Distill'n,°C	D86						
IBP		178	179	178	199	185	183
10%		193	198	198	246	204	203
50%		217	237	238	300	253	253
90%		256	310	311	332	321	321
FBP		300	334	335	345	340	339
% Recovery		98.9	98.8	98.9	98.8	98.8	98.2
Cetane No.	D613	39.2	42.1	39.2	48.8	44.5	38.8

TABLE 4.3.5: Properties of LCO Blends Treated with DII

		4.5MPa LCO Blend	4.5MPa MaxLCO Blend	10 MPa LCO Blend	10 MPa MaxLCO Blend
Blend Composition					
LSRD, vol%		72	77	62	71
LCO, vol%		28	23	38	29
	ASTM Method				
°API Gravity		35.1	37.3	34.0	37.4
Density	D1298	0.849	0.838	0.854	0.838
Flash Pt.,°C	D93	64	62	65	63
Cloud Pt.,°C	D2500	-33	-39	-27	-33
Pour Pt.,°C	D97	-45	-45	-45	-48
Viscosity @ 40°C, cst.	D445	1.70	1.58	1.83	1.57
Sulphur, wt%	D4294	0.24	0.17	0.20	0.10
Residue on 10% Bottoms,	D524				
wt% clear		0.22	0.42	0.28	0.26
wt% treated		0.16	0.30	0.46	0.27
Distill'n,°C	D86				
IBP		184	180	182	181
10%		197	194	197	195
50%		227	220	230	220
90%		284	266	285	266
FBP		336	324	324	317
% Recovery		98.2	98.5	98.8	98.2
% Residue		1.0	0.8	0.5	0.8
% Loss		0.8	0.7	0.7	1.0
Cetane No.	D613	38.0	38.0	42.6	37.9
+0.05%DII		39.7	40.7	45.8	39.6
+0.10%DII		41.8	42.3	44.3	41.0
+0.15%DII		41.5	43.3	44.9	42.8

Table 4.3.6: Product Data on Diesel Ignition Improver



"ETHYL" DIESEL IGNITION IMPROVER 3 DII-3

Product Bulletin

"ETHYL" DIESEL IGNITION IMPROVER 3 (DII-3)

Diesel ignition improvers are used to improve the cetane number ratings of diesel fuels. They offer refiners a means for meeting customer diesel fuel cetane number specifications without additional costly processing. They enable refiners to upgrade distillate stocks to diesel fuel quality.

Diesel fuel cetane numbers are indicative of the time that is required for a fuel to ignite following its injection into the engine cylinder—the higher the cetane number the shorter the delay period. The cetane number ratings for commercial diesel fuels normally range between 35 and 55.

The first commercial cetane improver introduced by Ethyl was DII, a mixture of primary amyl nitrates. Later DII-2, mixed primary hexyl nitrates, was made available. In a continuing effort to develop the most cost-effective products DII-3, octyl nitrate, now is offered.

The following is a comparsion of DII-2 and DII-3 physical properties:

TYPICAL COMPOSITIONS

	DII-2	DII-3
Total Nitrates	95	98

PHYSICAL PROPERTIES (TYPICAL)

	DII-2	DII-3
Form	Liquid	Liquid
Color	Pale Yellow	Pale Yellow
Water, wt %	0.05	0.05
Color, ASTM D 1500	1.0	1.0
Acid as HNO_3, wt %	0.003	0.003
Vapor Pressure, mm Hg		
20°C (68°F)	0.6	0.2
82°C. (180°F)	26.0	10.
137°C (279°F)		100.
Flash Point, TCC		
°C (°F)	59 (138)	72 (162)
Freezing Point °C (°F)	-97 (-143)	-50 (-58)
Density @ 20°C (68°F)		
g/ml	0.97	0.9640
lb/U.S. gal	8.09	8.04
Density Temperature Correction Factor		
g/ml per °C	0.00098	0.00093
g/ml per °F	0.00054	0.00052
Viscosity		
cSt @ 20°C (68°F)	1.29	1.8
cSt @ 0°C (32°F)	1.9	2.7
cSt @ -29°C (-20°F)	4.0	7.7
Solubility @ 20°C (68°F)		
In Diesel Fuel	Miscible	Miscible
Solubility of Water in Nitrate wt %		
@ 0°C (32°F)		0.025
@ 24°C (75°F)	0.04	0.042
Thermal Stability	Decomposition at 175°C (340°F)	Begins

EFFECTIVENESS

DII-2 and DII-3 were compared in five commercial diesel fuels covering a wide range of cetane numbers. The results are expressed in the volume percent of additive required for cetane number increases of 3 and 5 and the cetane number increase combined with 0.1 volume % additive.

Base Fuel Cetane Number	Vol. % Required for Cetane Number Increase: 3.0 Cetane No. DII-2	3.0 Cetane No. DII-3	5.0 Cetane No. DII-2	5.0 Cetane No. DII-3	Cetane No. Increase 0.1 vol. % additive: DII-2	DII-3
47	0.036	0.036	0.065	0.065	7.3	7.3
42	0.040	0.040	0.087	0.087	5.4	5.4
40	0.067	0.062	0.160	0.145	3.7	4.1
40	0.057	0.052	0.135	0.135	4.4	4.4
35	0.063	0.063	0.200	0.200	3.7	3.7

The two additives are essentially identical in effectiveness.

STORAGE STABILITY

Diesel fuels containing 0.15% of DII-2 and DII-3 were stored for twelve weeks at 43.5°C. The fuels were cooled to ambient temperature once each day to simulate field storage conditions. No significant change was observed in the gum, sediment or cetane numbers of the stored samples when compared with the original fuels.

TABLE 4.3.7 : Upgraded LCO (15 and 20 MPa) Blends

		15 MPa LCO Blends			20 MPa LCO Blends		
		Winter	Fall/S	Summer	Winter	Fall/S	Summer
Blend Composition							
LSRD, vol%		87	66	49.7	88.5	66	49.7
HSRD, vol%		--	24	40.3	--	24	40.3
LCO, vol%		13	10	10	11.5	10	10
	ASTM Method						
Blend No#		4729	4730	4731	4732	4733	4734
°API Gravity		40.6	40.6	38.7	37.3	41.0	38.9
Density	D1298	0.822	0.831	0.838	0.820	0.830	0.837
Flash Pt.,°C	D93	62	66	67	61	67	72
Cloud Pt.,°C	D2500	-42	-18	-15	-42	-21	-15
Pour Pt.,°C	D97	-45	-33	-24	-45	-39	-27
Viscosity @ 40°C, cst.	D445	1.57	2.04	2.44	1.54	2.03	2.48
Sulphur, wt%	D4294	0.1	0.20	0.26	0.10	0.20	0.26
Residue on 10% Bottoms, wt% clear	D524				0.13		0.17
Distill'n,°C	D86						
IBP		183	178	190	183	184	189
10%		195	196	208	195	199	208
50%		218	235	260	218	237	258
90%		253	307	322	253	311	320
FBP		289	335	339	289	336	339
% Recovery		99.2	98.5	98.1	99.3	99.0	98.9
Cetane No.	D613	45.1	47.0	47.9	46.4	47.6	48.6

TABLE 4.3.8: Upgraded MaxLCO (15/20 MPa) Blends

Blend Composition	ASTM Method	15/20 MPa MaxLCO Winter	Fall/S	Summer
LSRD, vol%		82	60	48
HSRD, vol%		--	23.3	38.8
MaxLCO, vol%		18	16.7	13.2
Blend No.		4726	4727	4728
°API Gravity		40.6	38.7	37.5
Density	D1298	0.822	0.831	0.837
Flash Pt.,°C	D93	62	70	68
Cloud Pt.,°C	D2500	-42	-18	-15
Pour Pt.,°C	D97	-45	-36	-21
Viscosity @ 40°C, cst.	D445	1.54	2.00	2.37
Sulphur, wt%	D4294	0.09	0.19	0.25
Residue on 10% Bottoms, wt% clear	D524		0.02	
Distill'n,°C	D86			
IBP		181	187	187
10%		194	200	205
50%		217	236	255
90%		253	324	320
FBP		291	334	338
% Recovery		99.1	98.9	98.6
Cetane No.	D613	43.0	47.8	49.0

Table 4.4.1: Properties of Katalco NM506 Catalyst

KATALCO 506 nickel-molybdenum-alumina extruded catalyst is designed for high demand hydrotreating jobs. It has excellent activity for both desulfurization and denitrogenation. In addition, it has high aromatic saturation ability. KATALCO 506 is particularly recommended for hydrotreating heavy oils, cracked stocks, and for FCC pretreating.

TYPICAL CHEMICAL ANALYSIS, WT. %, DRY BASIS

MoO_3	27.0%
NiO	6.7%
Alumina Base	Balance

TYPICAL PHYSICAL PROPERTIES

Form	Extrudate	
Size	1/10" (Nom 1/8")	1/16"
Surface Area, sq m/gm	220	220
Total Pore Volume, ml/gm	0.39	0.39
Compacted Density, gm/cc	0.92	0.92
Reactor Loaded Density, lb/cu ft	54	54
Strength, lb Crush	14	14
Attrition Index*	97	97

**% retained on a 20-mesh sieve after tumbling for one-half hour*

HANDLING

Avoid eye and skin contact. Do not take internally.

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TABLE 4.4.2: Phase 1 Pilot Runs on Reprocessing HCCG

Run #		Feed	2045	2046	2047	2048
Sample #		--	300	385	385	385
WABT, °C		--	4.1	10.3	10.3	10.3
Pressure, MPa		--	2.0	2.0	1.0	2.0
LHSV			33	176	273	204
H_2 Consumed m^3/m^3						
Product Properties						
Density, @15°C		0.8247	0.8232	0.7906	0.7791	0.7929
Smoke Point, mm			--	21.2	23.2	22.2
Cloud Point, °C			--	<-55	<-55	<-55
Distillation						
D86, °C						
	10%	148	145	137	135	137
	30%	150	147	140	137	140
	50%	152	149	143	140	143
	70%	155	150	147	145	147
	90%	161	157	154	153	154
Composition, M.S. vol%						
Paraffins		22.2	27.1*	20.9	20.2	21.1
Naphthenes		20.4	19.5	60.0	72.8	58.8
Aromatics		57.4	53.4	19.1	7.0	20.1
n-paraffins		0.0	10.8	0.0	0.0	0.0
isoparaffins		22.2	16.3	20.9	20.2	21.1
cyclopentanes		0.5	2.0	3.8	2.2	4.8
cyclohexanes		16.0	15.5	53.8	67.8	51.4
dicycloparaffins		3.9	2.0	2.4	2.8	2.6
alkylbenzenes		56.7	53.4	19.1	7.0	20.1
tetralins		0.7	0.0	0.0	0.0	0.0

* inconsistent results, possibly bad sample

TABLE 4.4.3: Phase 2 Pilot Runs; Reprocessing HCCG

Run #	Feed	6010	6012	6014	6016	6018
WABT, °C	--	385	385	385	385	385
Pressure, MPa	--	10.3	10.3	10.3	10.3	10.3
LHSV	--	1.0	1.5	2.0	2.5	1.9
H_2 Consumed m^3/m^3	--	168.6	154.2	135.0	124.8	113.1
Product Properties						
Density, @15°C	0.825	0.777	0.783	0.789	0.793	0.80
Smoke Point, mm	--	31.2	25.6	21.5	19.5	21.7
Cetane No.		30.4	29.4	27.9	26.7	27.6
Distillation						
D86, °C IBP	136	129	127	132	129	132
10%	143	134	134	136	135	137
30%	147	138	137	141	139	140
50%	151	143	141	145	143	143
70%	156	149	147	151	148	149
90%	166	162	159	162	163	161
FBP	181	183	180	182	178	187
Composition, M.S. vol%						
Paraffins	23.9	28.1	28.8	29.8	30.7	30.2
Olefins	18.7	--	--	--	--	--
Napthenes	15.3	63.3	57.0	49.3	44.7	50.1
Aromatics	42.1	8.6	14.3	20.8	24.6	19.7
n-paraffins		7.6	6.9	6.2	6.7	6.4
isoparaffins		20.5	21.9	23.6	24.0	23.7
cyclopentanes		7.1	6.5	5.6	5.3	7.4
cyclohexanes		53.1	47.4	40.6	36.3	38.8
dicycloparaffins		3.1	3.1	3.1	3.1	3.9
alkylbenzenes		8.5	14.2	20.7	24.3	19.5
tetralins		0.1	0.1	0.2	0.3	0.2

TABLE 4.4.4: Reprocessed HCCG Evaluated as Jet Fuel Type B

Property	ASTM	CGSB Spec.	Reprocessed HCCG
Freeze Point, °C	D2386	-51 (max.)	-68
Reid Vapour Pressure, kPa	D323	21 (max.)	0.8
Flash Point, °C	D93	----	21
Conductivity, pS/m	D3114	50 - 450	needs additive
Distillation, °C	D86		
10%			137
20%		143 (max.)	138
50%		188 (max.)	143
90%		243 (max.)	161
FBP			187
% recovered at 204°C			
Residue, vol%		1.5 (max.)	0.3
Distillation Loss, vol%		1.5 (max.)	0.4
Density, kg/L @ 15°C	D1298	0.750 - 0.801	0.803
Aromatics, vol%	D1658	25 (max.)	19.7
Olefins, vol%	D1319	5 (max.)	0.0
Sulphur, wt%	D3227	0.4 (max.)	21 ppm
Sulphur, Mercaptans, wt%		0.003 (max.)	0
Copper Corrosion	D130	No. 1 (max.)	1
Net Heat of Combustion, MJ/kg	D3338	42.8 (min.)	43.5
Luminometer No.	D1740	45 (min.)	48
Thermal Stability	D3241		
JFTOT colour		3 (max.)	1
pressure drop, kPa		3.4 (max.)	0

Figure 2.0.1 Model Refinery Layout

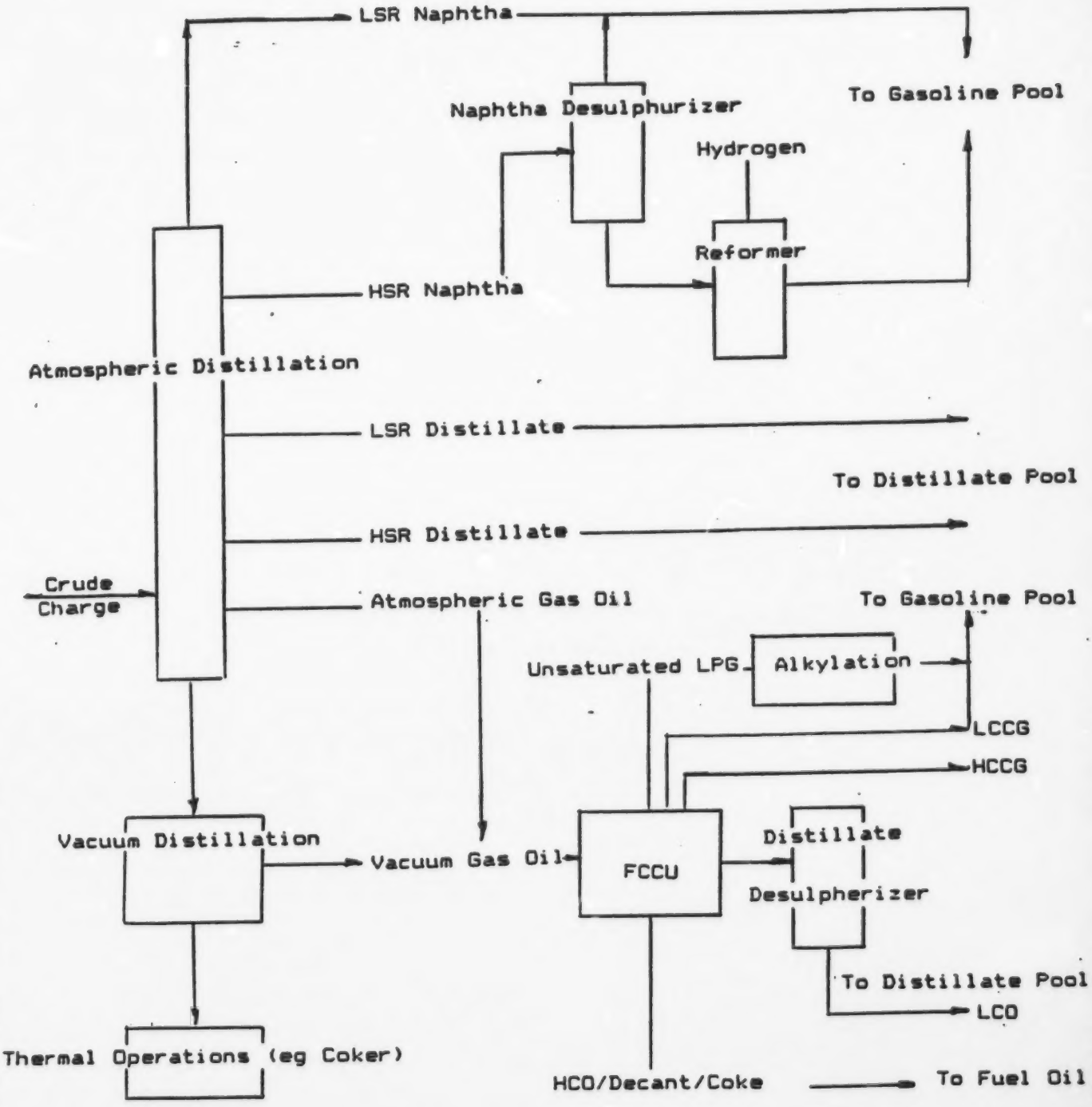


Figure 3.3.1: P&ID for P-12 Minireactor System

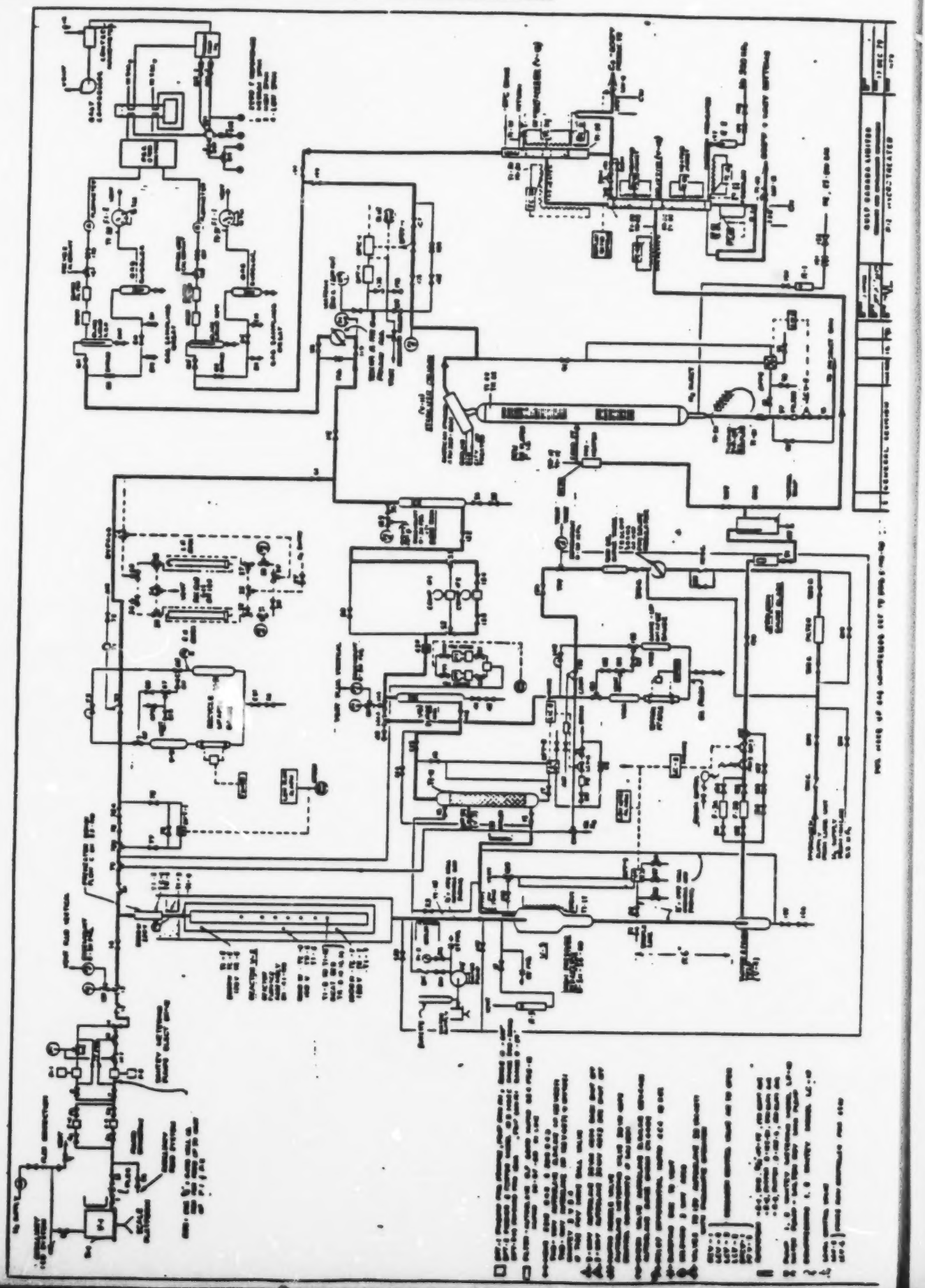


Figure 3.3.2: P&ID for P-16 Minireactor System

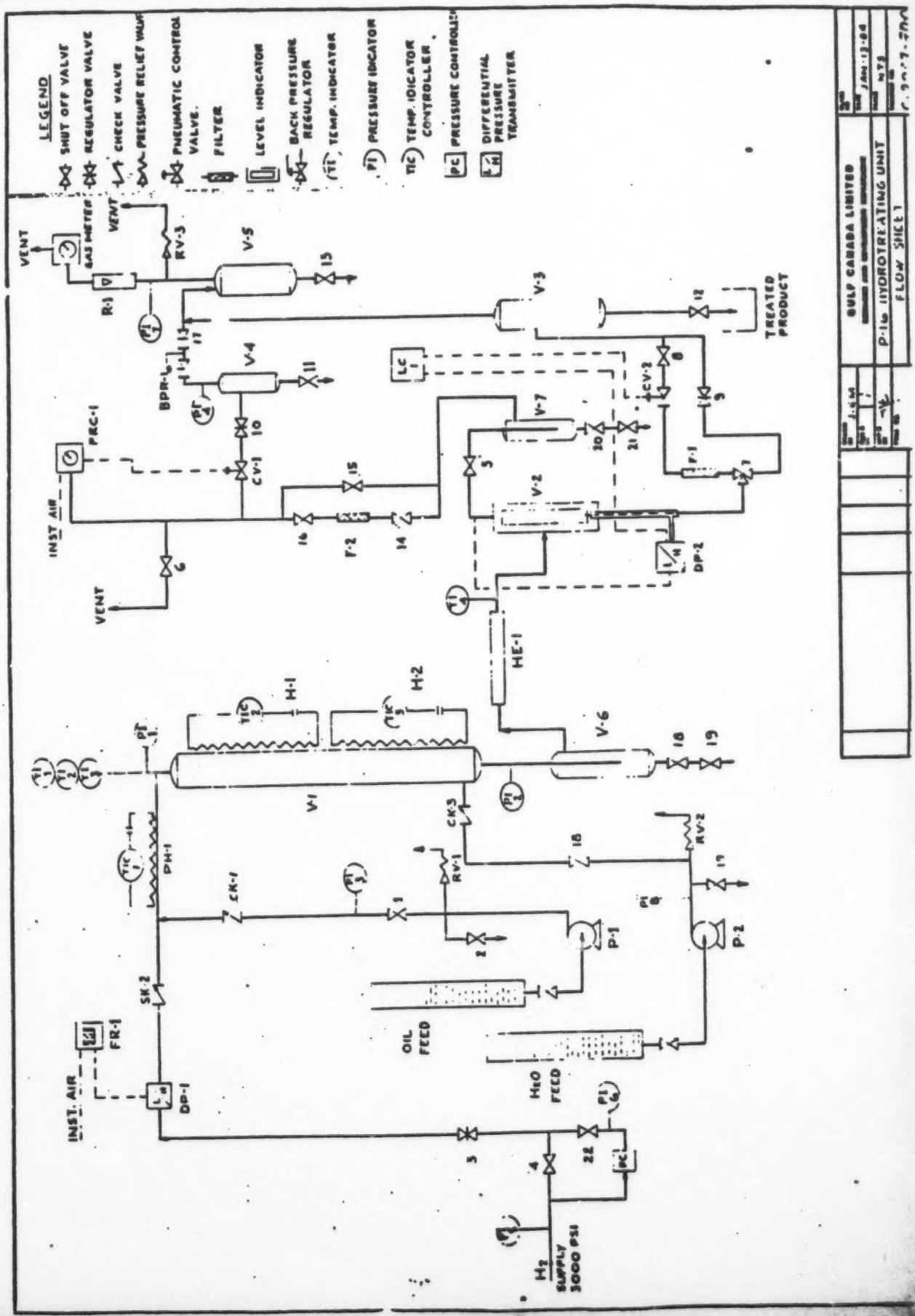


Figure 3.3.4: Example of Pilot Plant Log Sheet

RUN NO. 045 CHARGE STOCK D83-118 ARCD-1 (90-167°C FCCG)
SHEET NO. 2 CHARGE SP. GR. 400/0.8247
PROJECT NO. 407-83-65 CATALYST NM-506
RFD SIZE 54", 301 lg, 322.7 oc

GULF OIL CANADA LIMITED - RESEARCH AND DEVELOPMENT
E-12 HYDROCRACKING UNIT (ARC UNIT)

DAY 84-05-24
OPERATORS 24-8
8-16 AL
16-24

TIME 00:45	LIQUID FLOW RATES: CHARGE RATE cm³/hr	CHARGE PUMP STROKE %	PRODUCT RATE cm³/hr	PRODUCT A.P.I.	PRODUCT Density kg/m³ @ 15°C	GAS FLOW RATES: COMP SETTINGS (1) / (2)	SHAFT GAUGES: INLET PRESS kPa	SHAFT GAUGES: OUTLET PRESS kPa	REACTOR GAS: H₂ Purity mole %	REACTOR GAS: H₂ Flow SCFB	STABILIZER: INJ GAS Flow L/hr	STABILIZER: %	STABILIZER: H₂/HC	H₂ Consumption SCFB	H₂ Purity to Gas Chrom %	Reactor Pressure kPa	Ambient Temp °C	TIME
01	532	7.15	3169	40.2	.8231	6.45				29.8								01
02																		02
03	1067						13.6	27.1		49.1							25	03
04																120.0		04
05	1059						13.5	31.4								120.0	751.9	23	05
06							13.8	32.1		49.0								06
07	1058	"	3157	40.4	.8238	"	13.8	15.5		50.0						120.0	75.5	25	07
08																		08
09	1060	"				"	13.8	36.7		50.1						120.0	753.3	23	09
10																		10
11	1059	"				"	13.7	37.5		50.8						120.0	753.3	22	11
12																		12
13	1062	"	3166.3	40.4	.8238	"	13.7	39.4		50.6						120.0	753.4	24.5	13
14																		14
15	1058	"				"	13.8	38.8		49.3						120.0	752.8	26.0	15
16																		16
17	1057	"					13.7	31.4		49.1						120.0	752.1	26.5	17
18																		18
19	1055	"	3164	40.4	.8231		13.7	28.5		49.9						120.0	751.4	26.1	19
20	548																	20
21	548						13.6	30.4		50.8							752.2	25.8	21
22																		22
23	1062						13.5	27.2		51.4							752.5	24.0	23
24																	752.2	24.6	24

TIME 00:45	TEMPERATURES °C: REACTOR P/B T1-2	TRANSFER LINE T1-4	FURNACE T8-5	FURNACE T8-6	FURNACE T8-7	T1-3	T1-5	REACTOR T2-1	T2-2	T2-3	T2-4	T2-5	REACTOR OUTLET CONDENSER T1-16	H.P. SEP. T1-15	STABILIZER P/B TIC-5	STABILIZER TOP T8-10	STABILIZER BOTTOM T8-11	STABILIZER REBOILER T1-11	STABILIZER REBOILER T1-12	STABILIZER BOTTOMS COOLER T1-13	STABILIZER BOTTOMS COOLER T1-14	PRESSURES kPa: FEED DISCH P1-3/P1	REACTOR INLET P2-4/P2-7	DRIER INLET P1-3/P1-4	COMP INLET P1-5	COMP OUTLET P1-6	STAB OFF GAS P8-2	H.P.S. CYL PRESS	TIME
01																													01
02	228	254	309	308	308			300		300	300	300	301	300.2	156								4.27	.02	4.25	4.46			02
03	237	250	309	308	308			299		300	300	300	301	300	155								4.23	.02	4.21	4.42			03
04																													04
05	212	241	309	308	308			300		300	300	300	301	300.2	153								4.24	.02	4.22	4.42			05
06																													06
07	259	254	309	308	308			299		300	300	300	301	300	155								4.21	.01	4.20	4.30			07
08																													08
09	218	250	309	308	308			300		301	301	300	301	300.6	152								4.31	.01	4.30	4.50			09
10																													10
11	227	252	309	308	308			299		300	300	300	301	300.0	148								4.23	.02	4.21	4.41			11
12																													12
13	236	253	309	308	308			299		300	300	300	301	300.0	152								4.30	.02	4.28	4.49			13
14																													14
15	237	250	309	308	308			299		300	300	300	301	300.0	153								4.22	.03	4.19	4.41			15
16																													16
17	238	249	309	308	307			299		300	300	300	301	300.0	154								4.27	0.03	4.24	4.45			17
18																													18
19	238	252	309	308	307			299		300	300	300	301	300.0	154								4.31	0.02	4.29	4.50			19
20																													20
21	243	249	309	308	307			299		300	300	300	301	300.0	155								4.29	0.01	4.28	4.48			21
22																													22
23	247	251	309	308	308			299		300	300	300	301	300.0	152								4.29	0.02	4.27	4.48			23
24																													24

Fig. 4.2.1: AROMATIC CONVERSION IN LCO UPGRADING

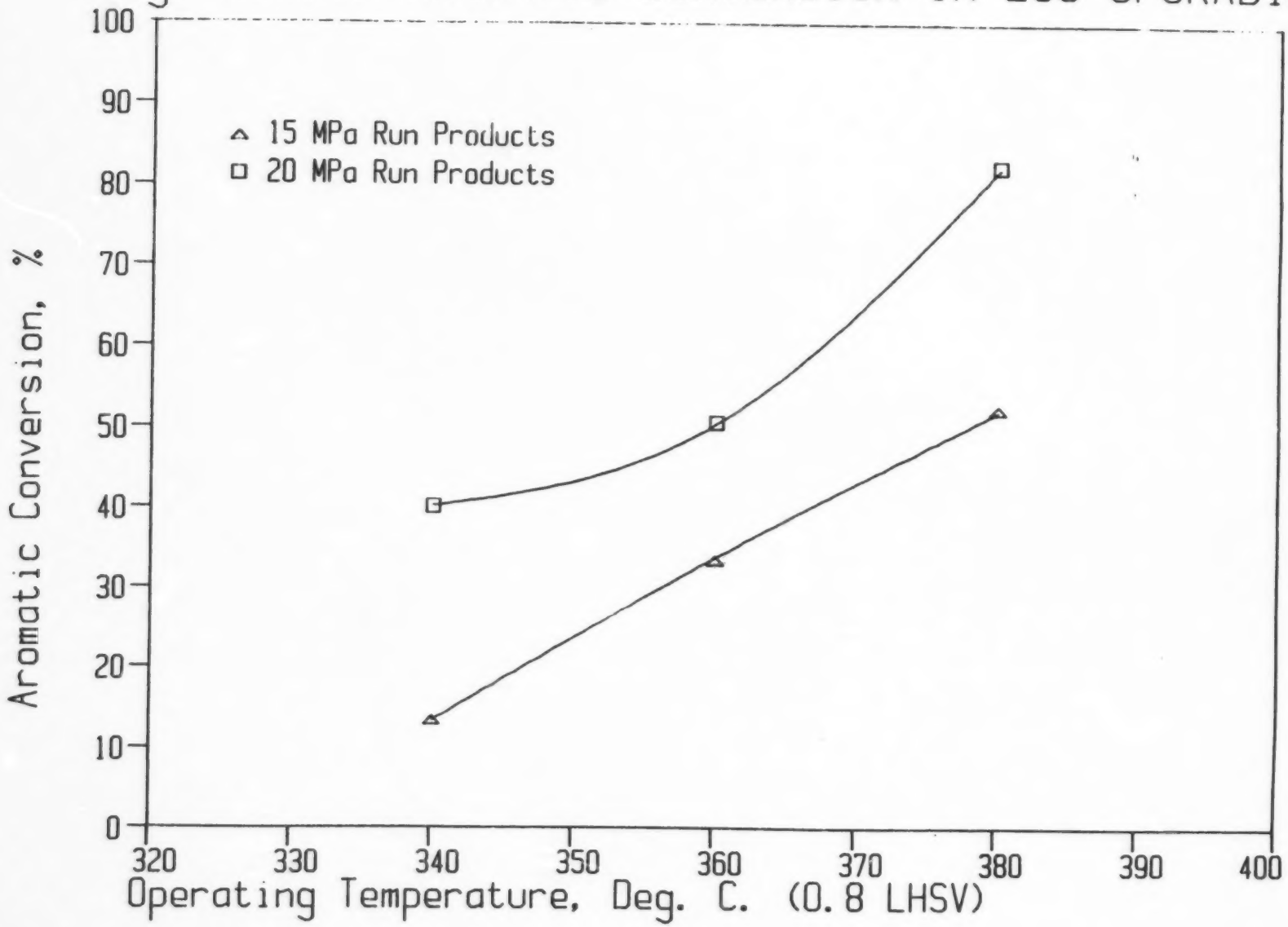


Fig. 4.2.2: AROMATIC CONVERSION IN MLCO UPGRADING

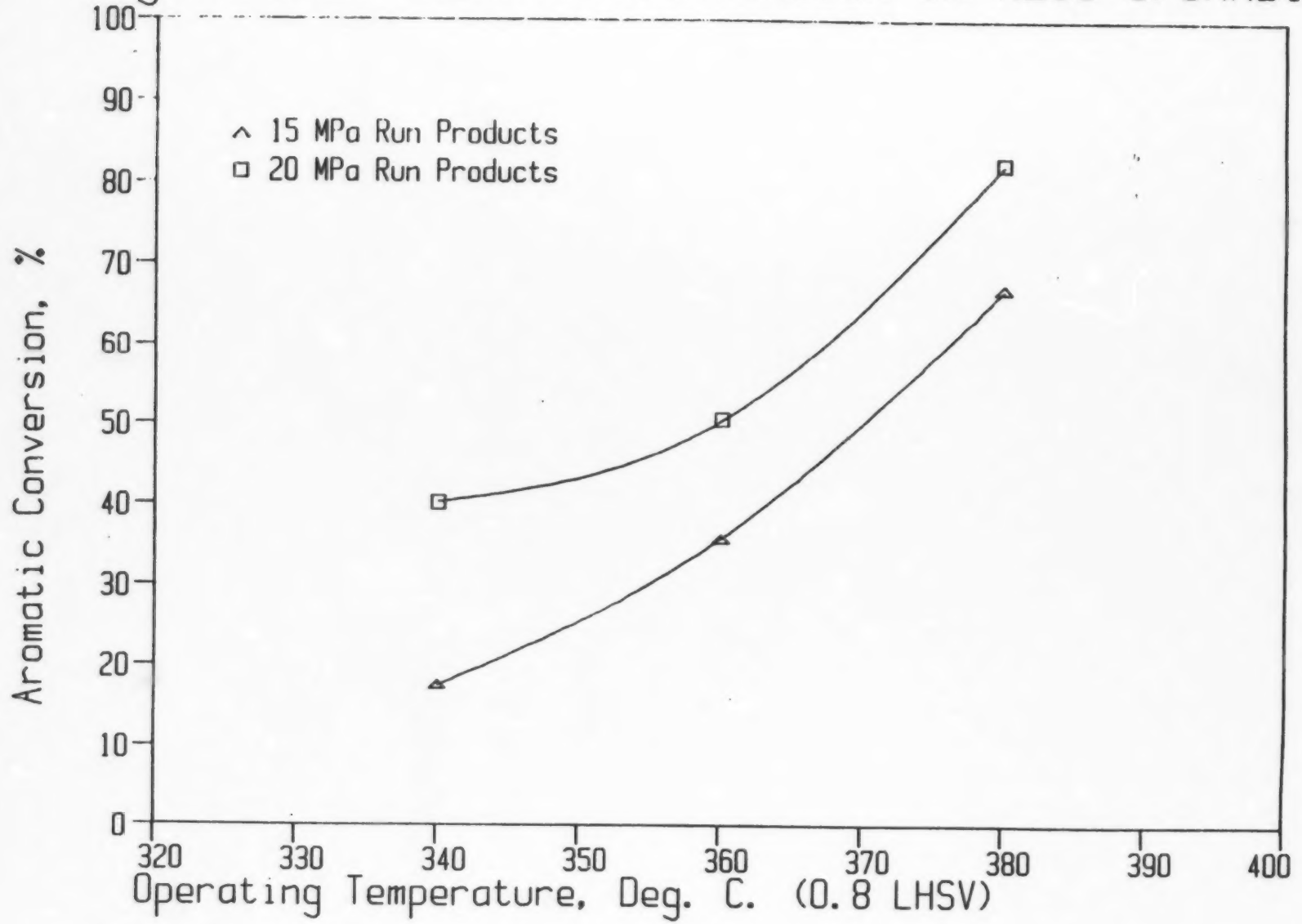


Fig. 4.2.3: 15 MPa LCO PRODUCT COMPOSITIONS

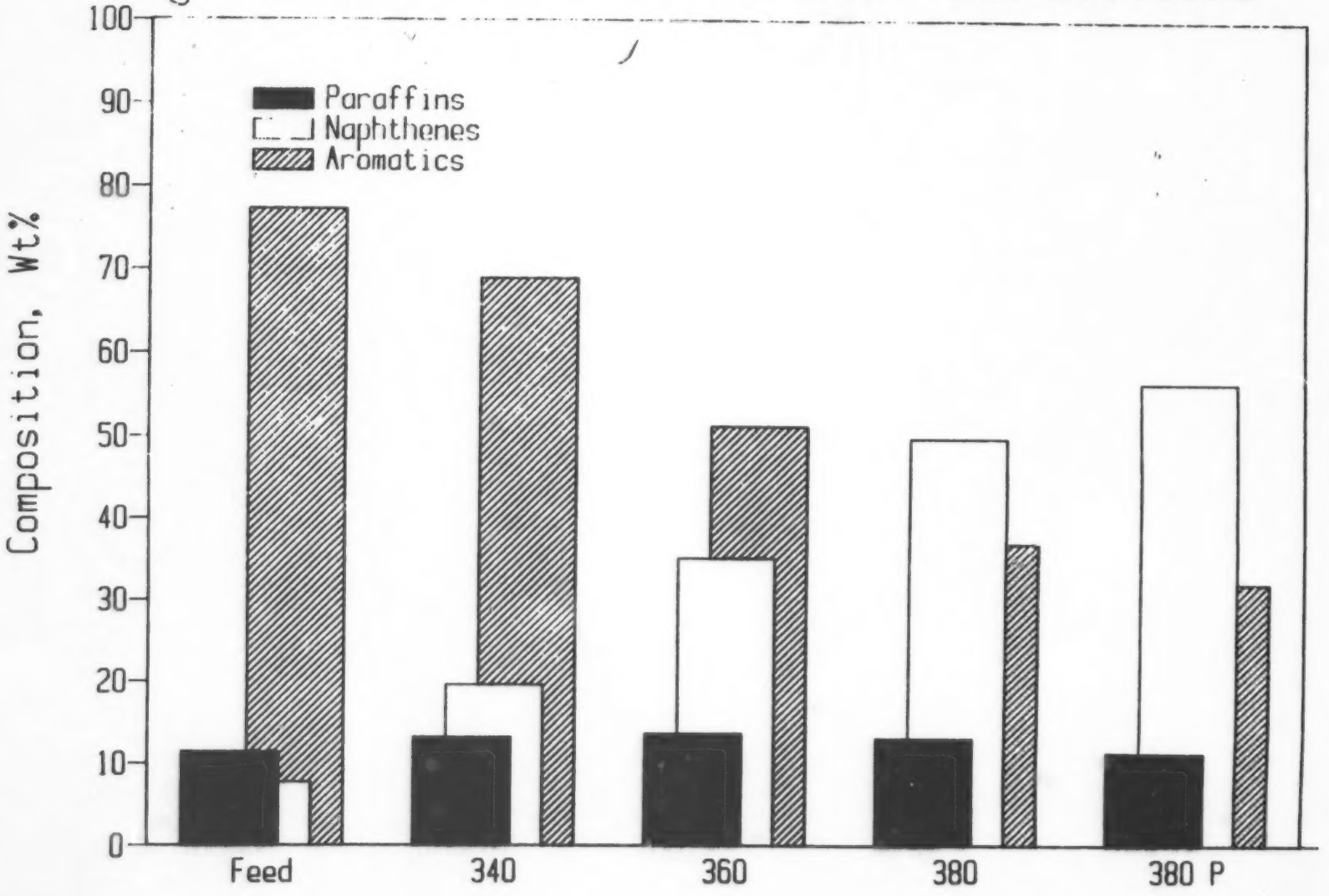


Fig. 4.2.4: 15 MPa MLCO PRODUCT COMPOSITION

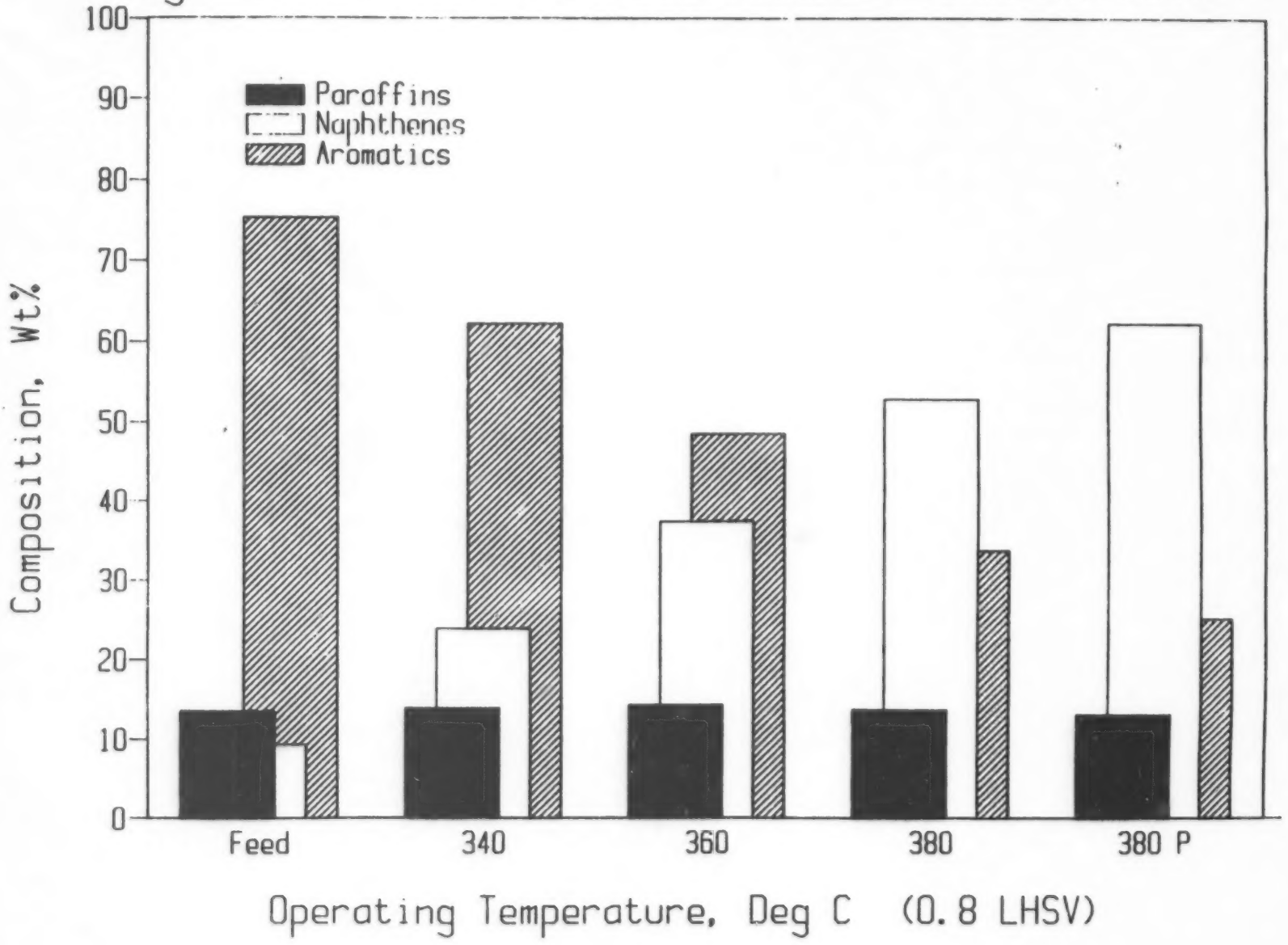


Fig. 4.2.5: 20 MPa LCO PRODUCT COMPOSITIONS

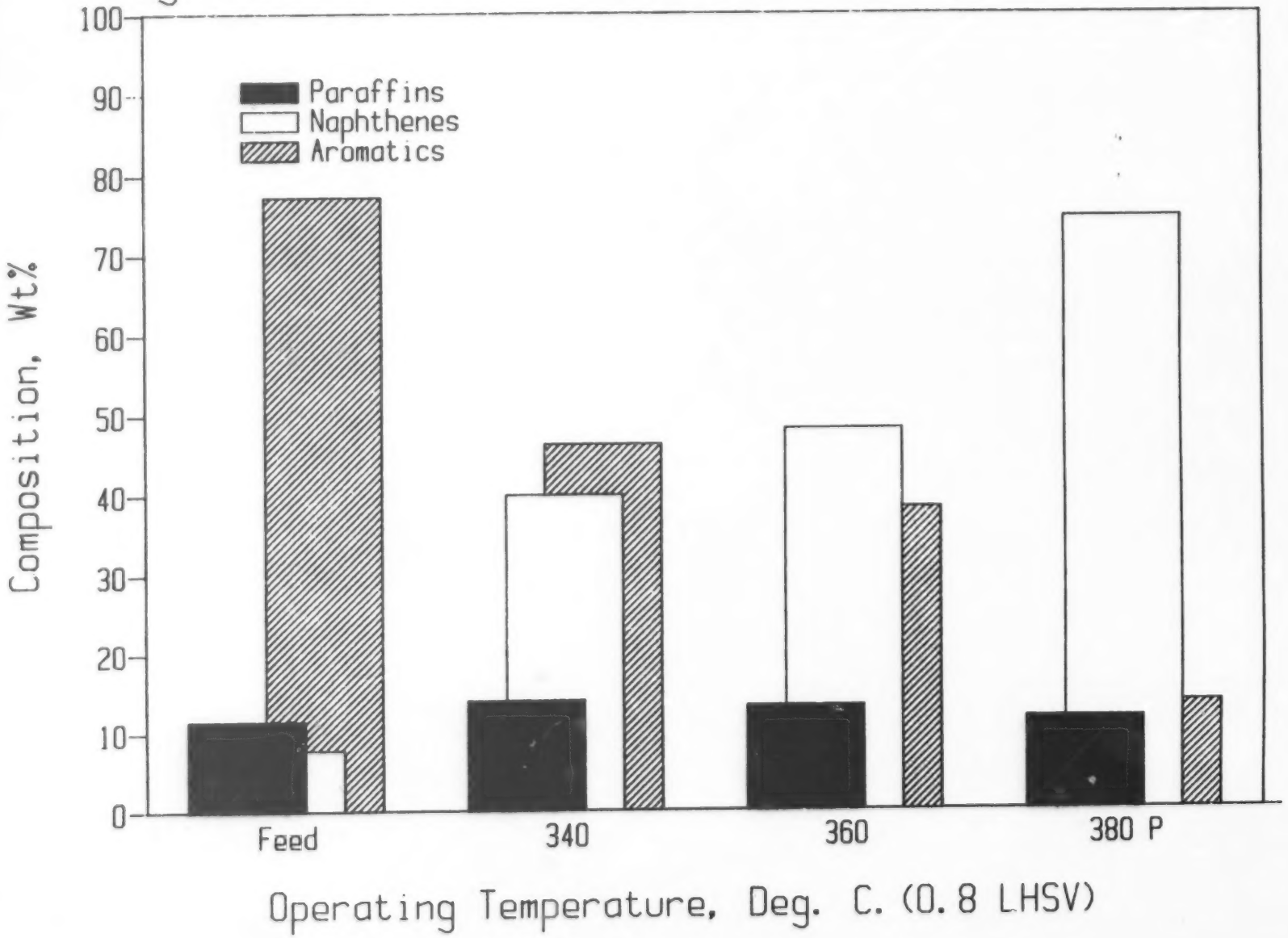


FIG. 4.2.6: 20 MPa MLCO PRODUCT COMPOSITION

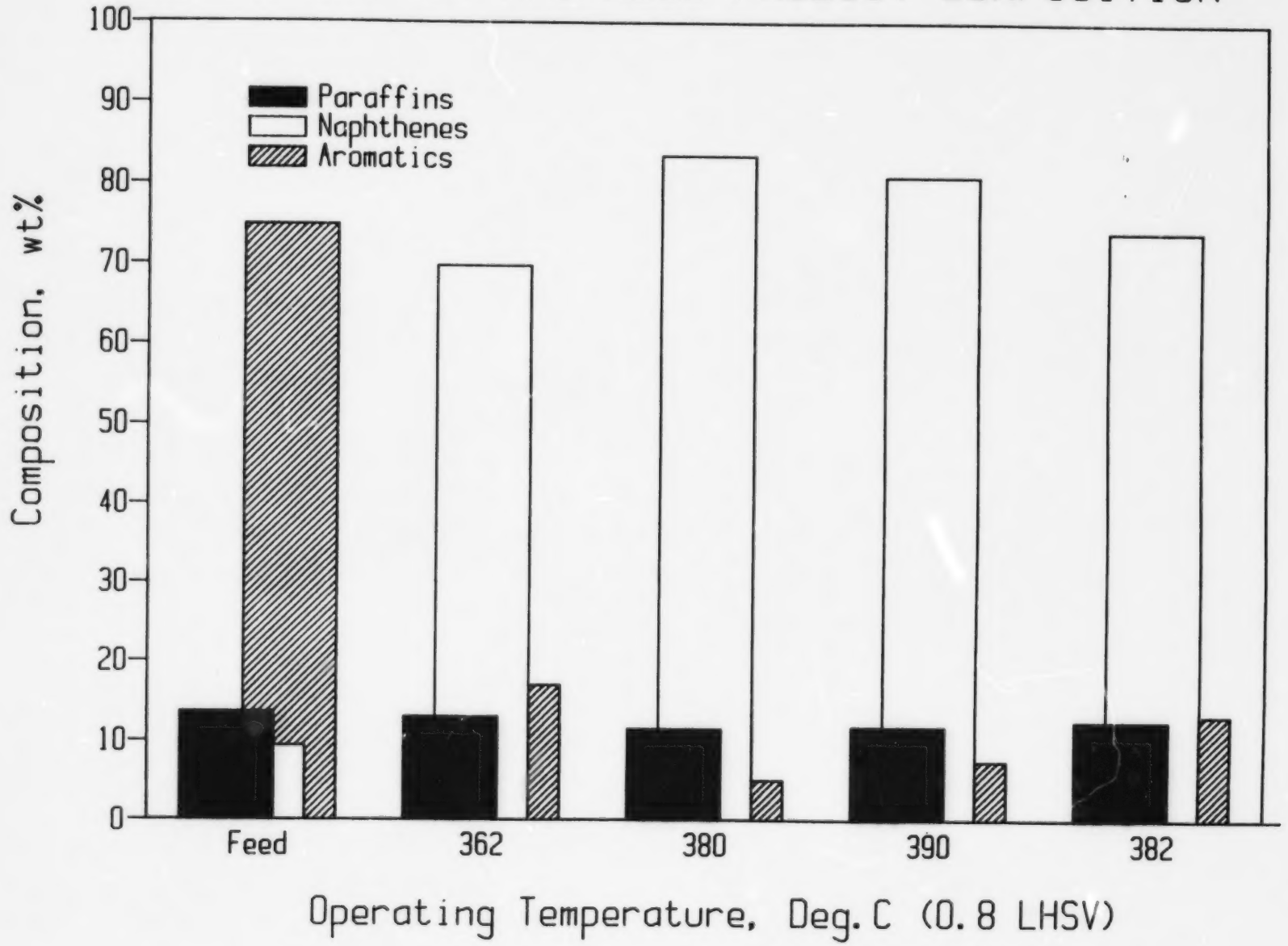


Fig. 4.2.7: CETANE vs MONOAROMATICS in PRODUCTS

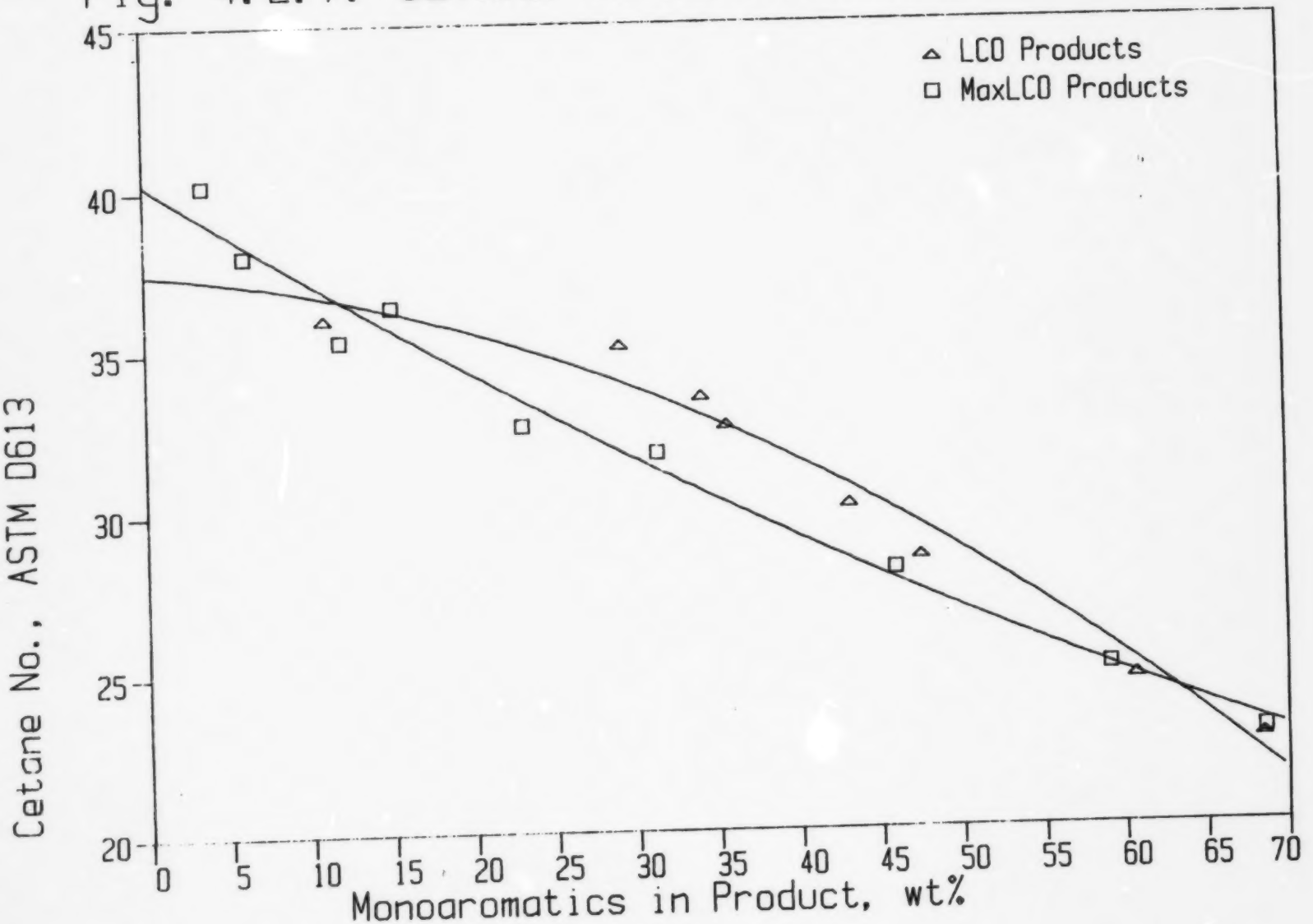


Figure 4.3.1: Refinery Production Ratios

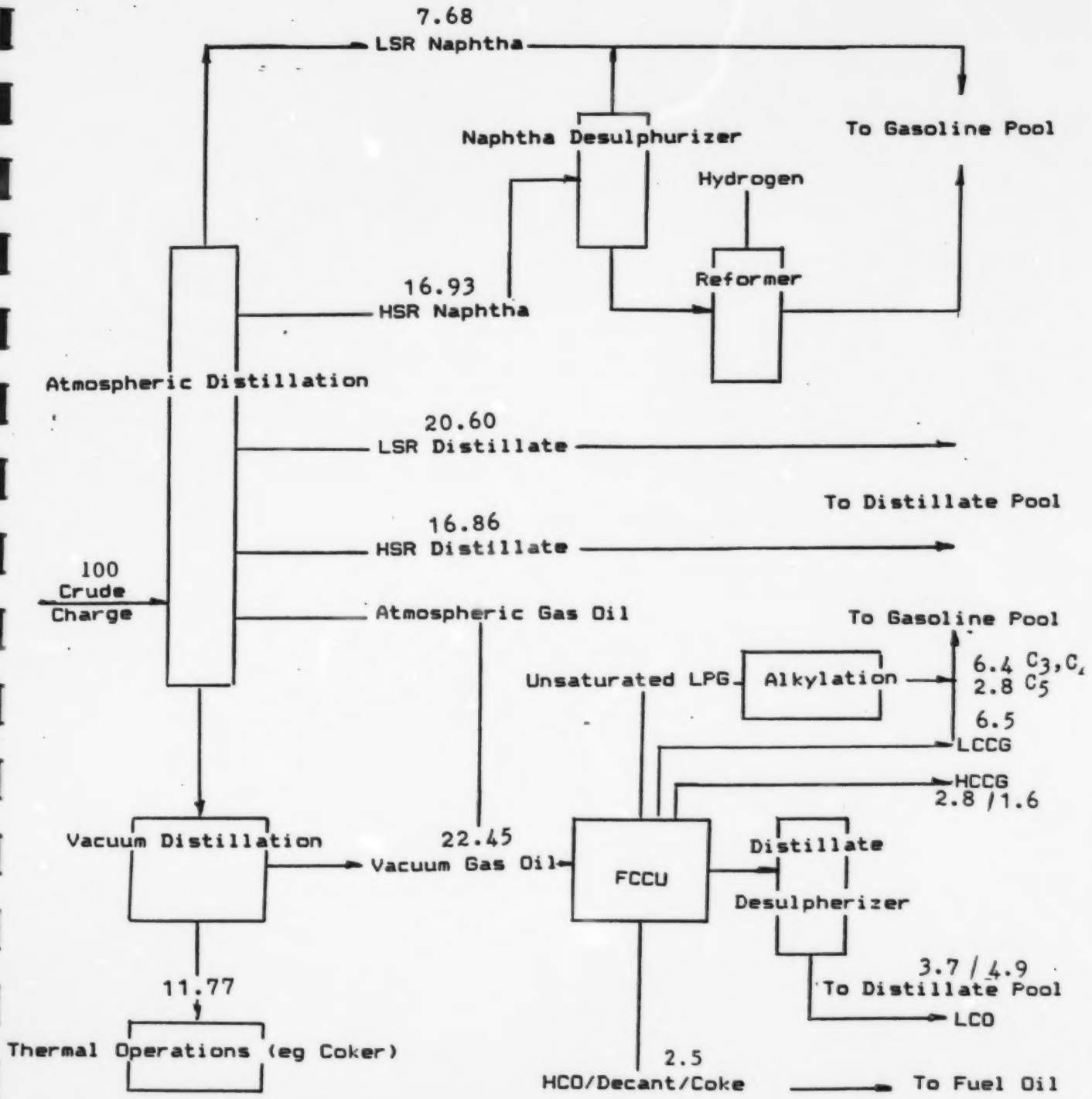


Figure 4.3.2: Triangular Co-ordinate Blending Diagram
For 200-360 C, 4.5 MPa HTLCO

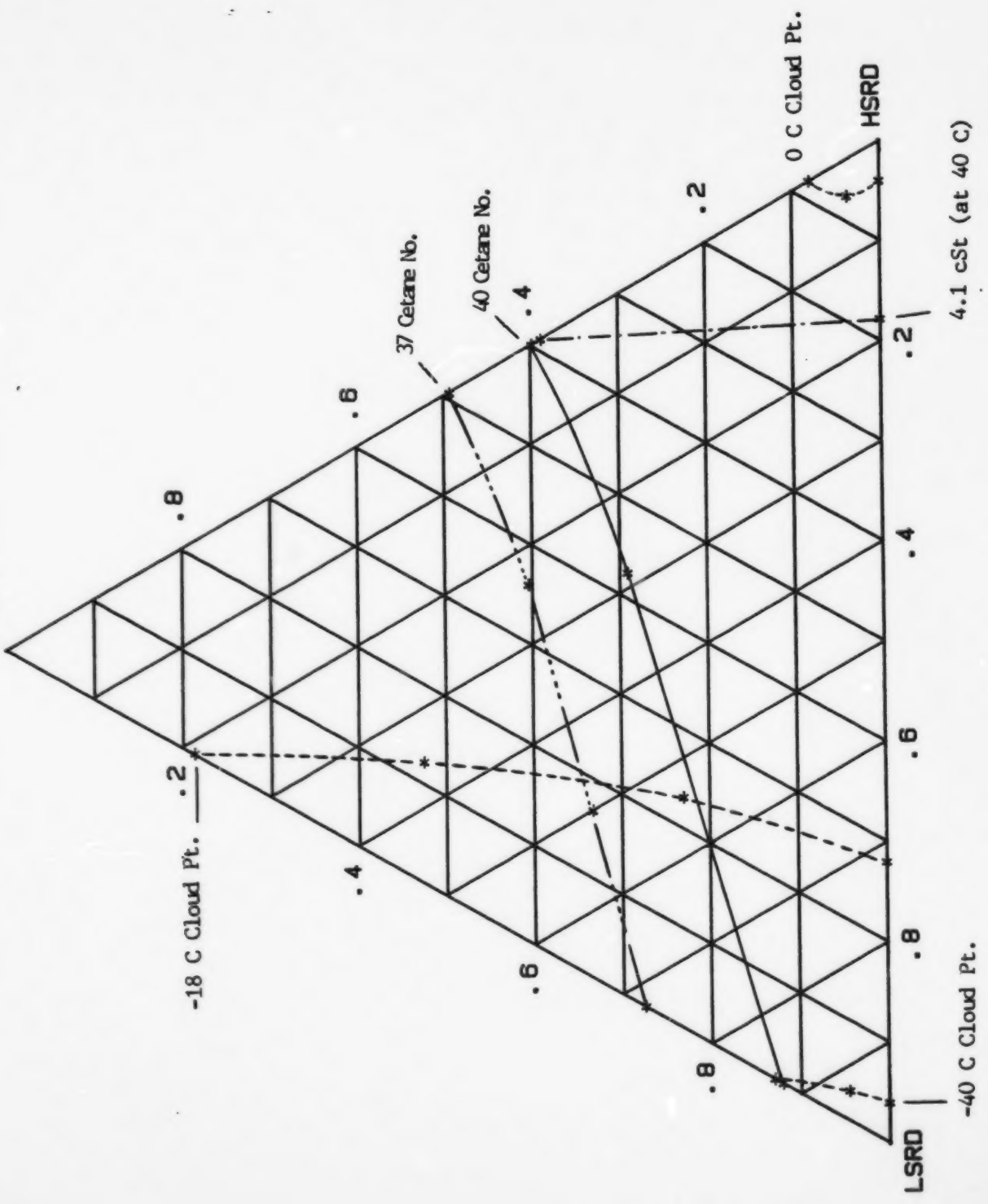


Figure 4.3.3: Triangular Co-ordinate Blending Diagram
For 167-360 C, 4.5 MPa HTLCO

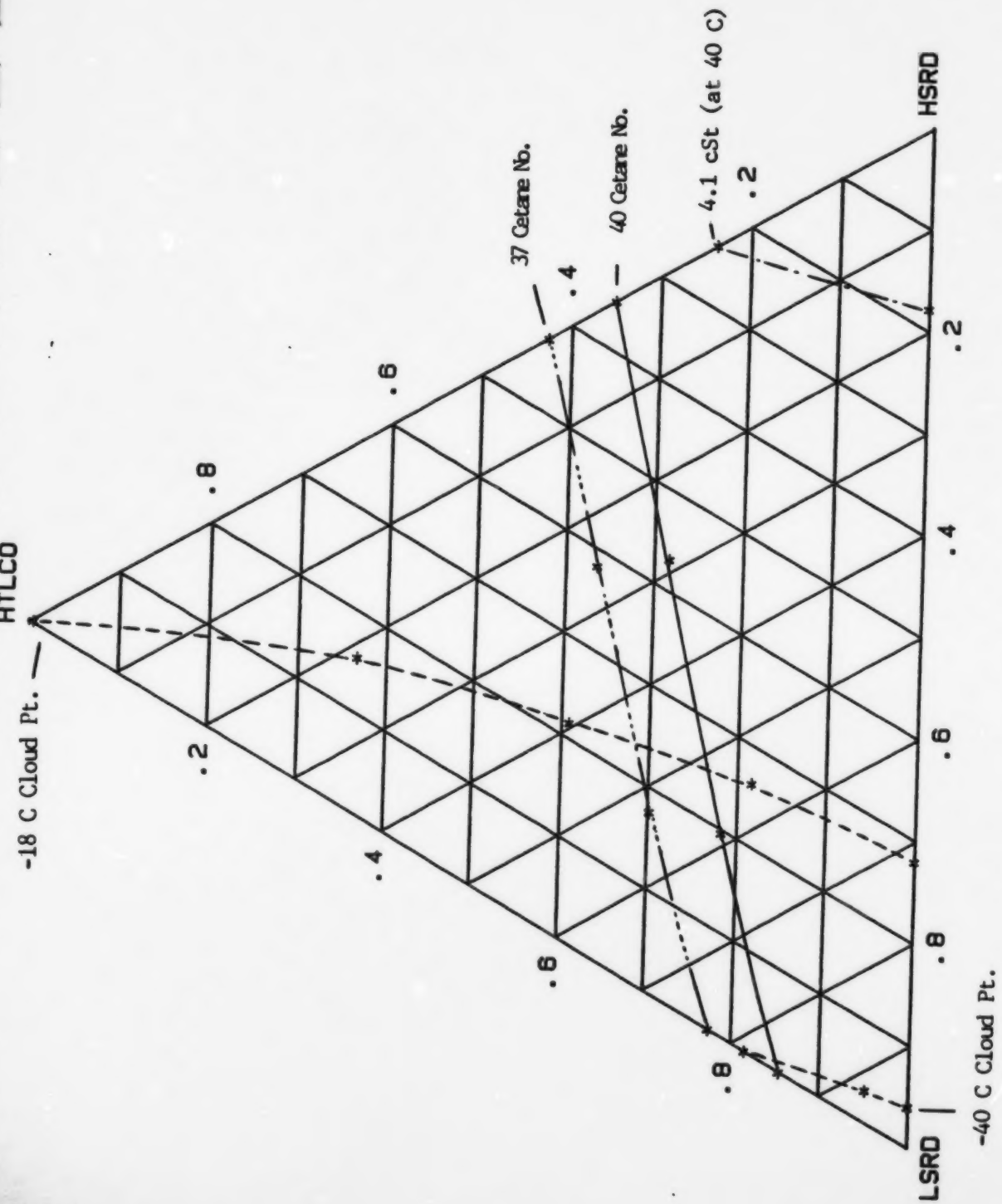


Figure 4.3.4: Triangular Co-ordinate Blending Diagram
For 200-360, 10 MPa HTLCO

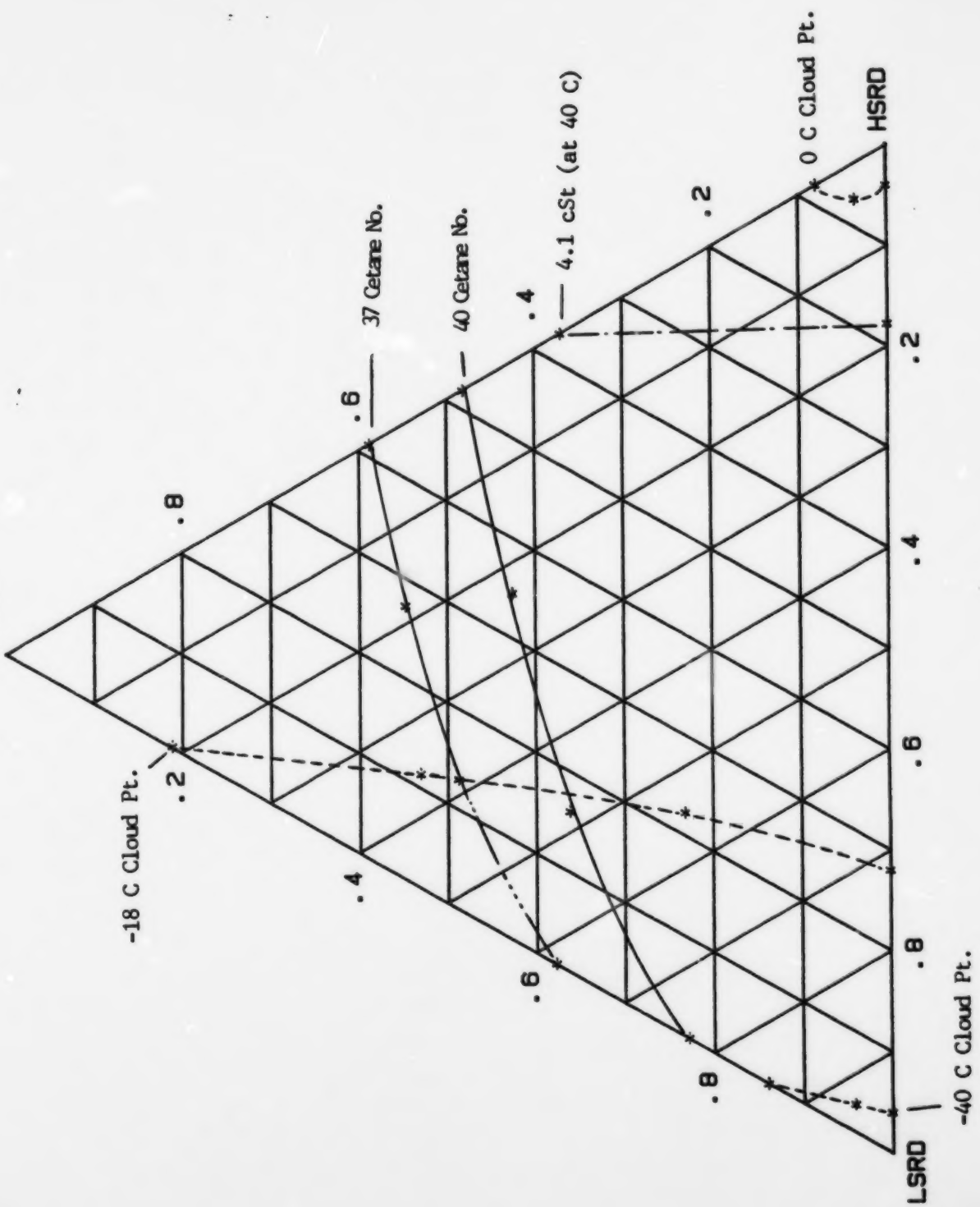


Figure 4.3.5: Triangular Co-ordinate Blending Diagram
For 167-360 C, 10 MPa HTLCO

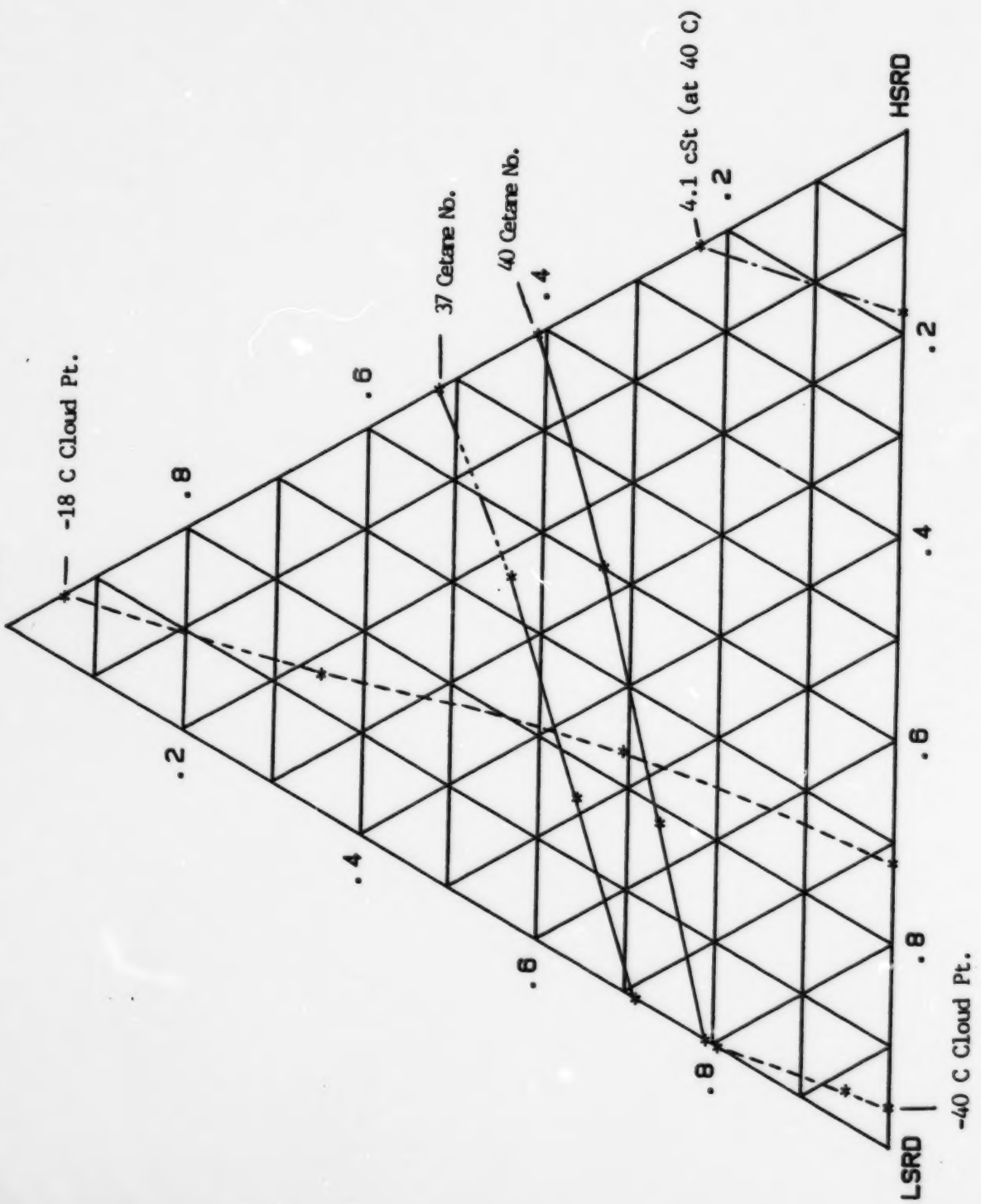


Figure 4.3.6: Triangular Co-ordinate Blending Diagram
For 200-360, 15 MPa HTLCO

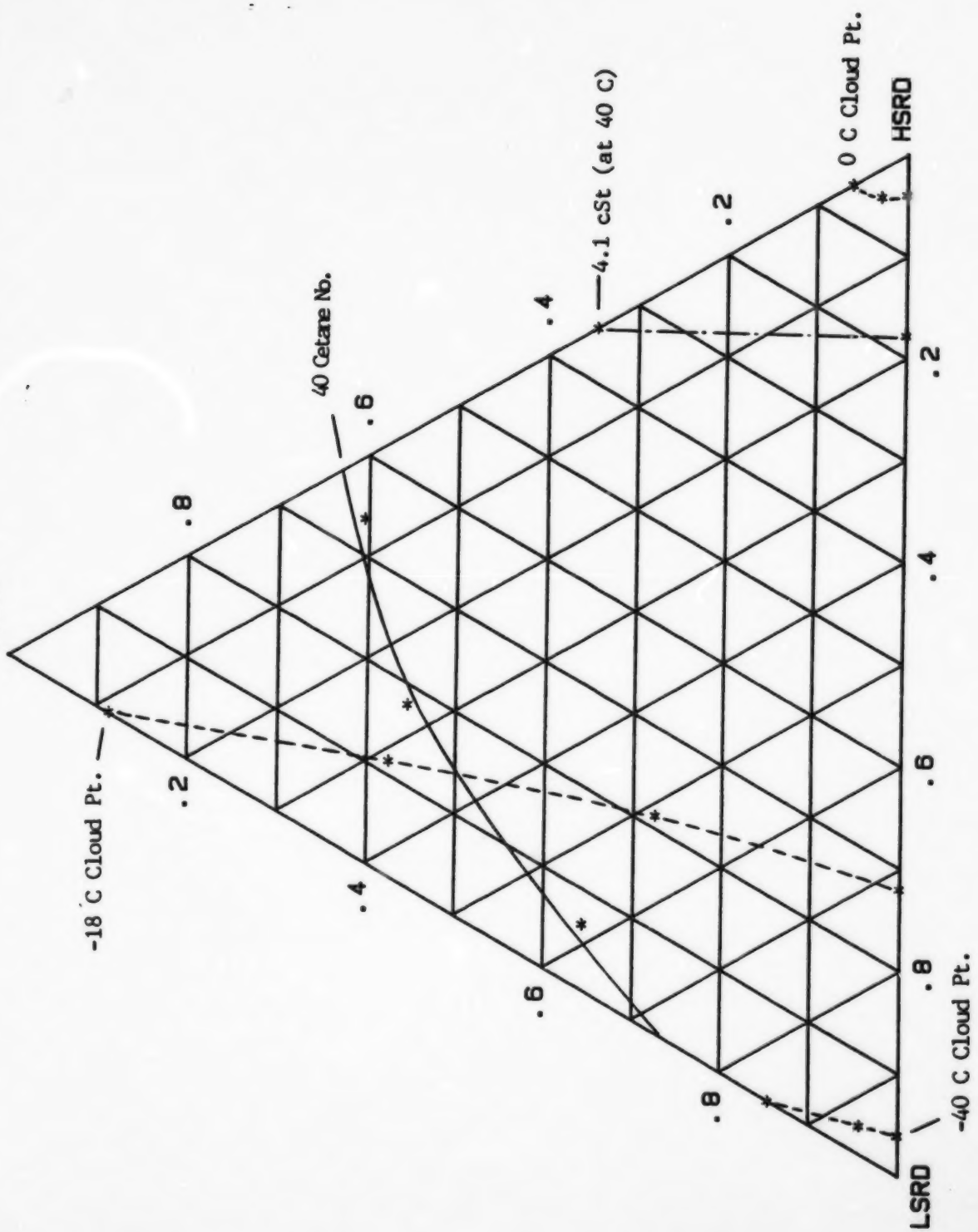


Figure 4.3.7: Triangular Co-ordinate Blending Diagram
for 200-360 C, 20 MPa HTLCO

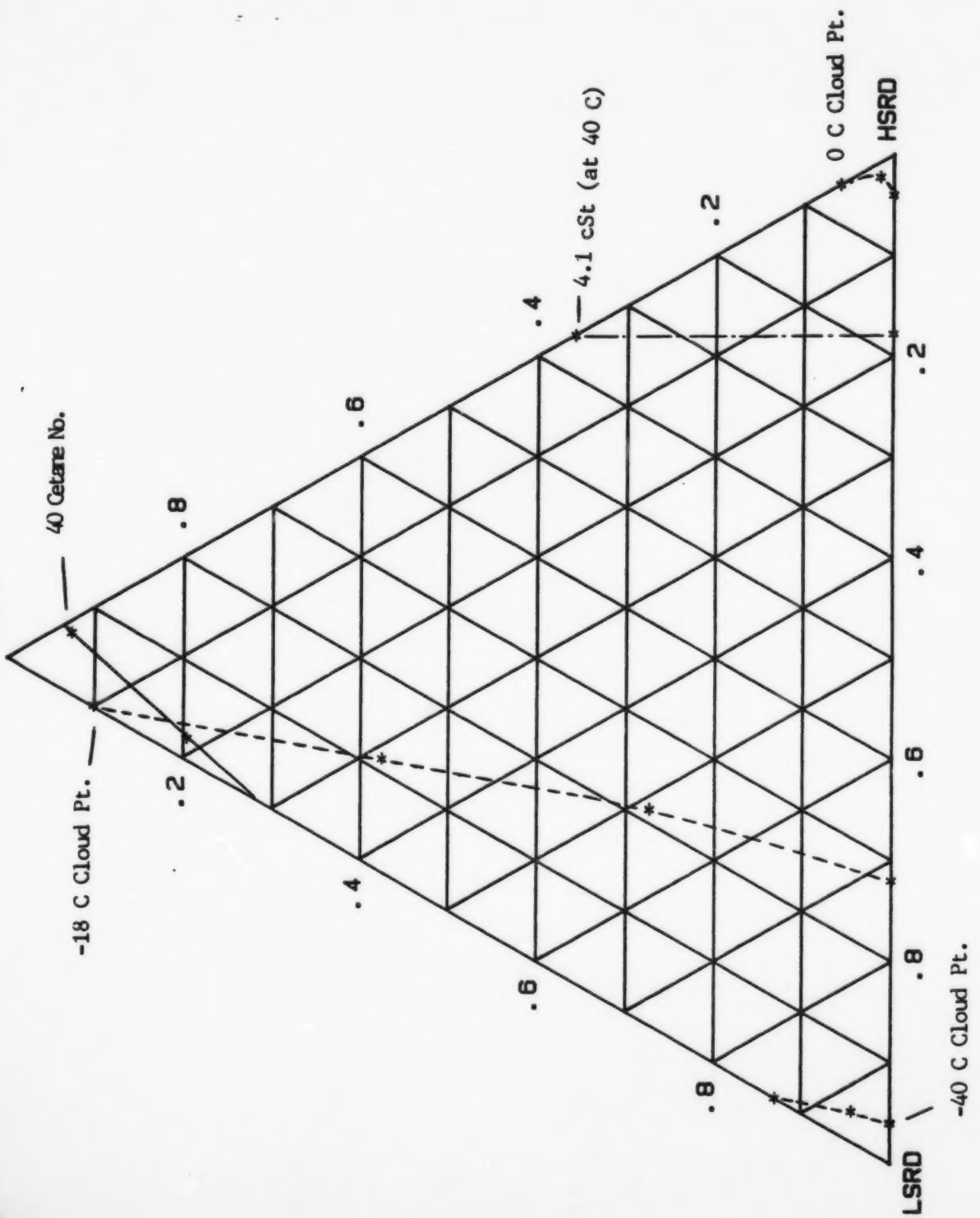


Figure 4.3.8: Triangular Co-ordinate Blending Diagram
For 167-360 C, 15/20 MPa HTLCO

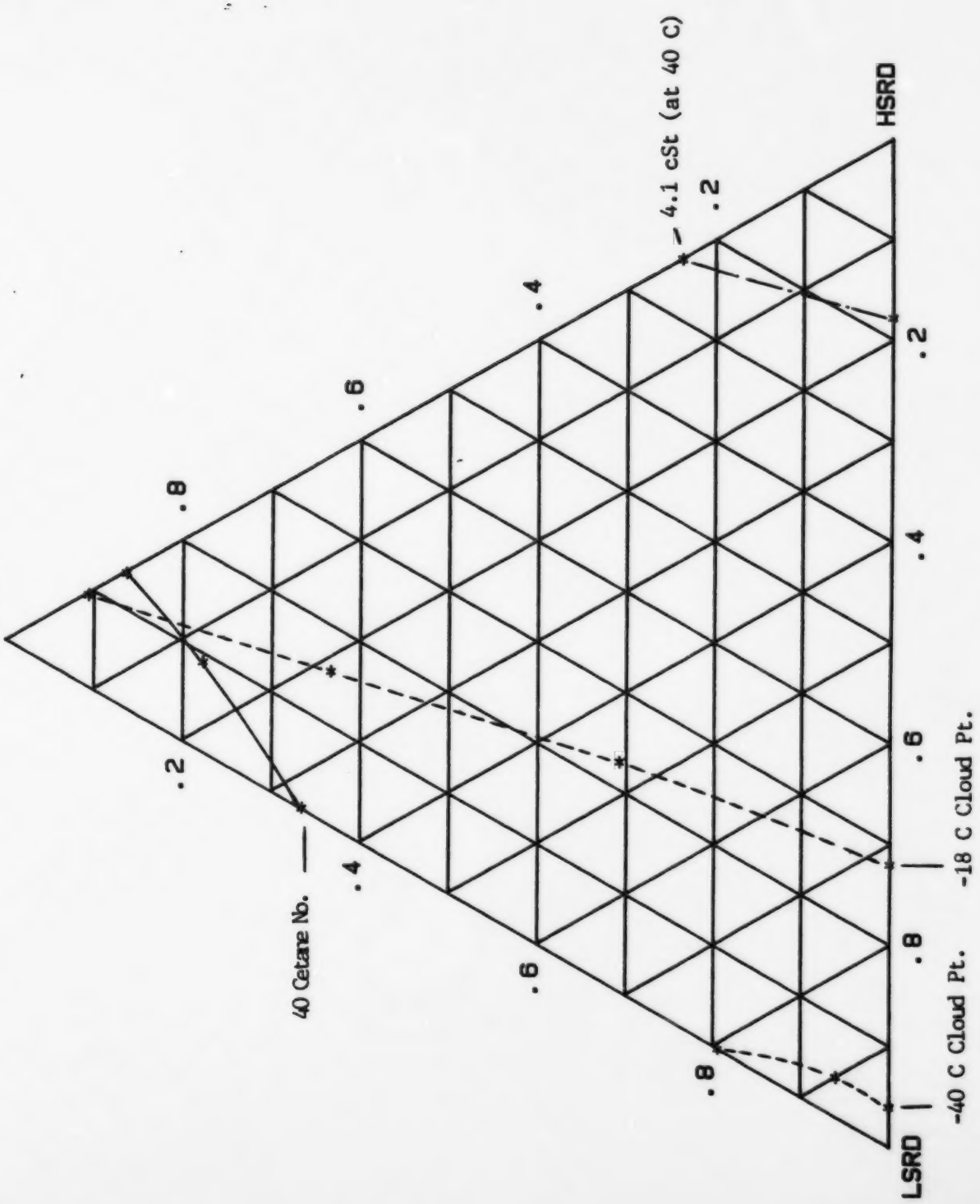


FIGURE 4.3.9 CETANE RESPONSE OF 4.5MPa LCO BLENDS

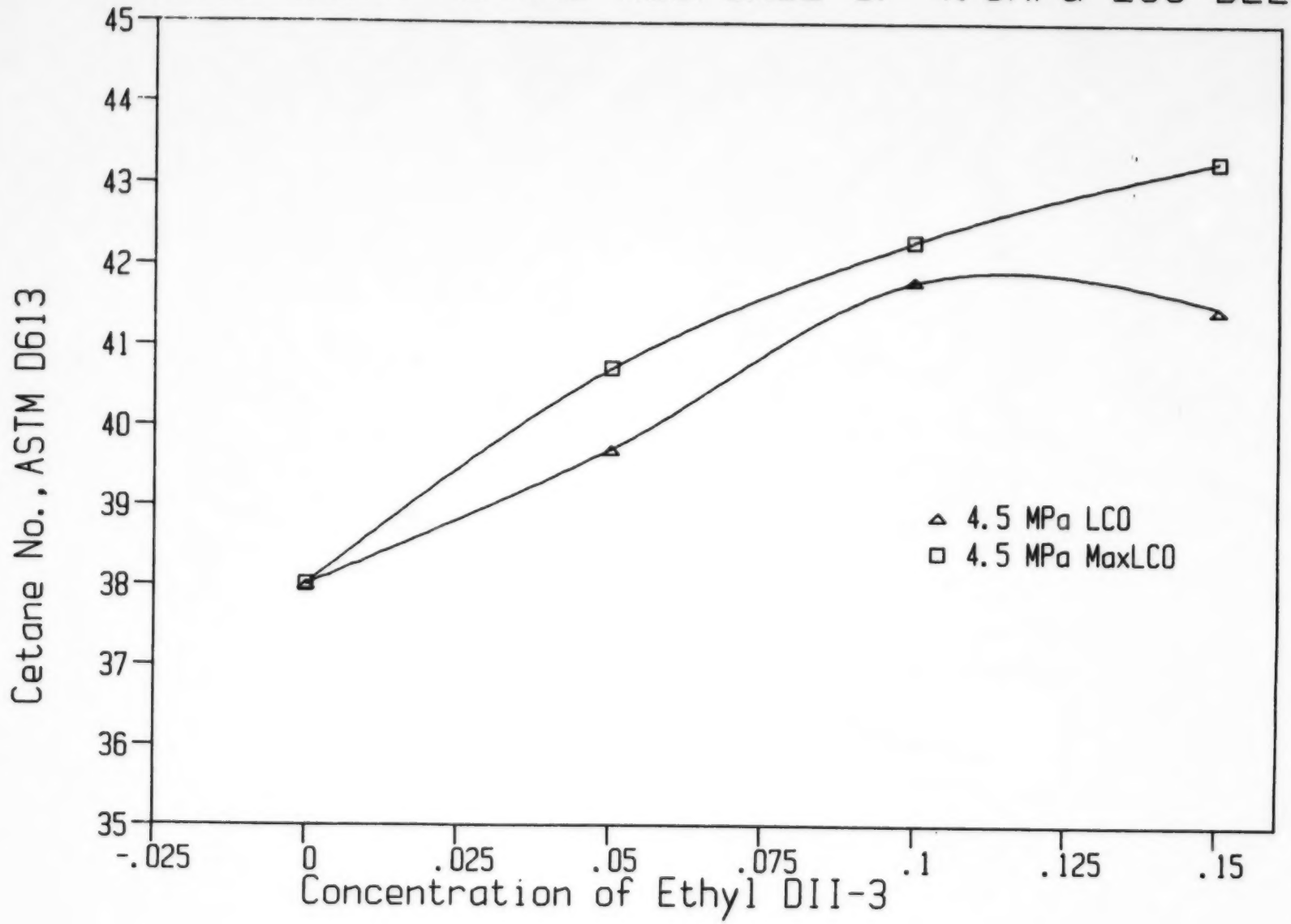


FIGURE 4.3.10 CETANE RESPONSE OF 10 MPa LCO BLENDS

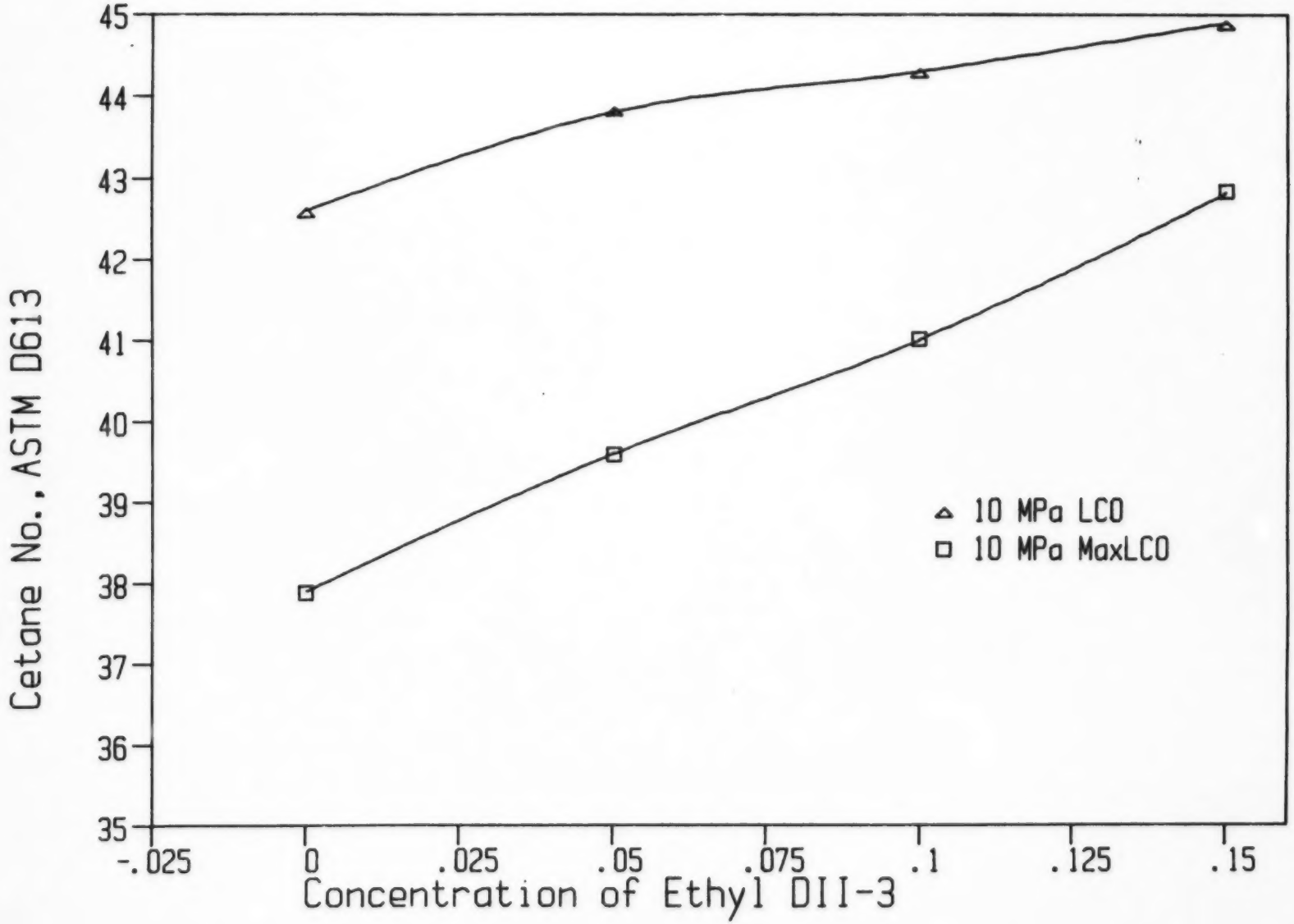


FIG. 4. 4. 1 CLARKSON HCCG BROMINE NO. VS TEMPERATURE

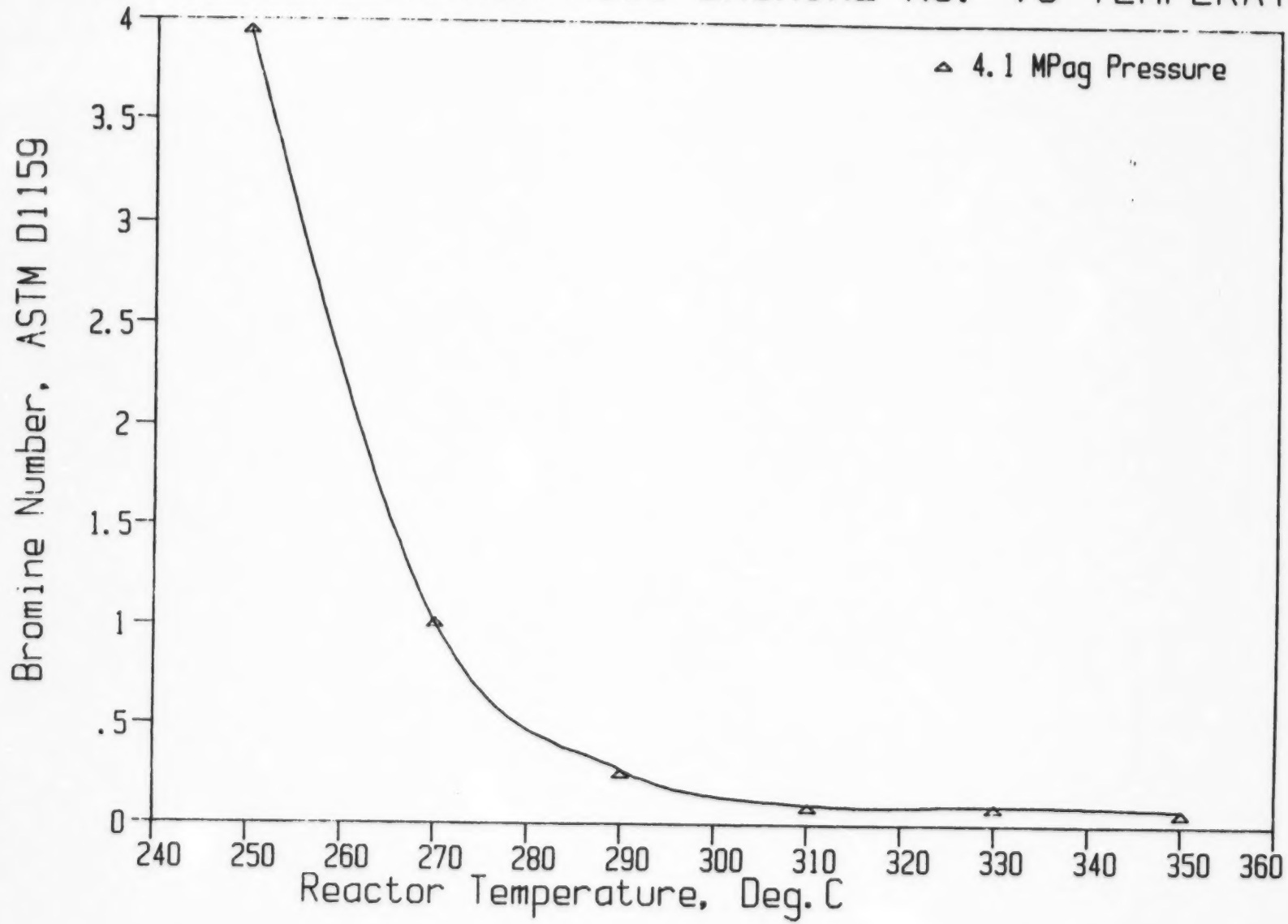


FIG. 4.4.2 CLARKSON HCCG AROMATICS VS TEMPERATURE

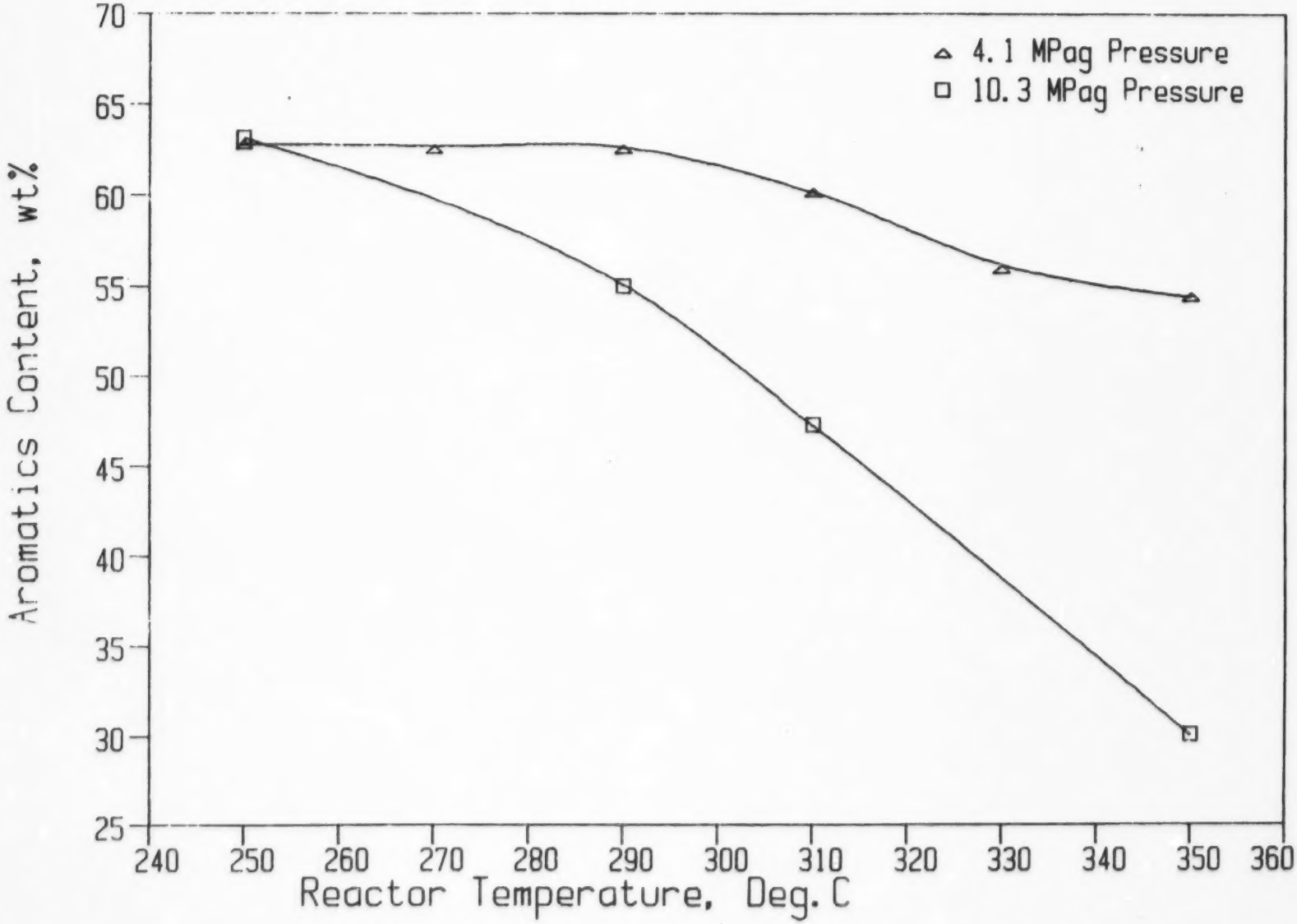


Figure 4.4.3: Evaluation of Heat Balance in Single Stage HCCG Reprocessing

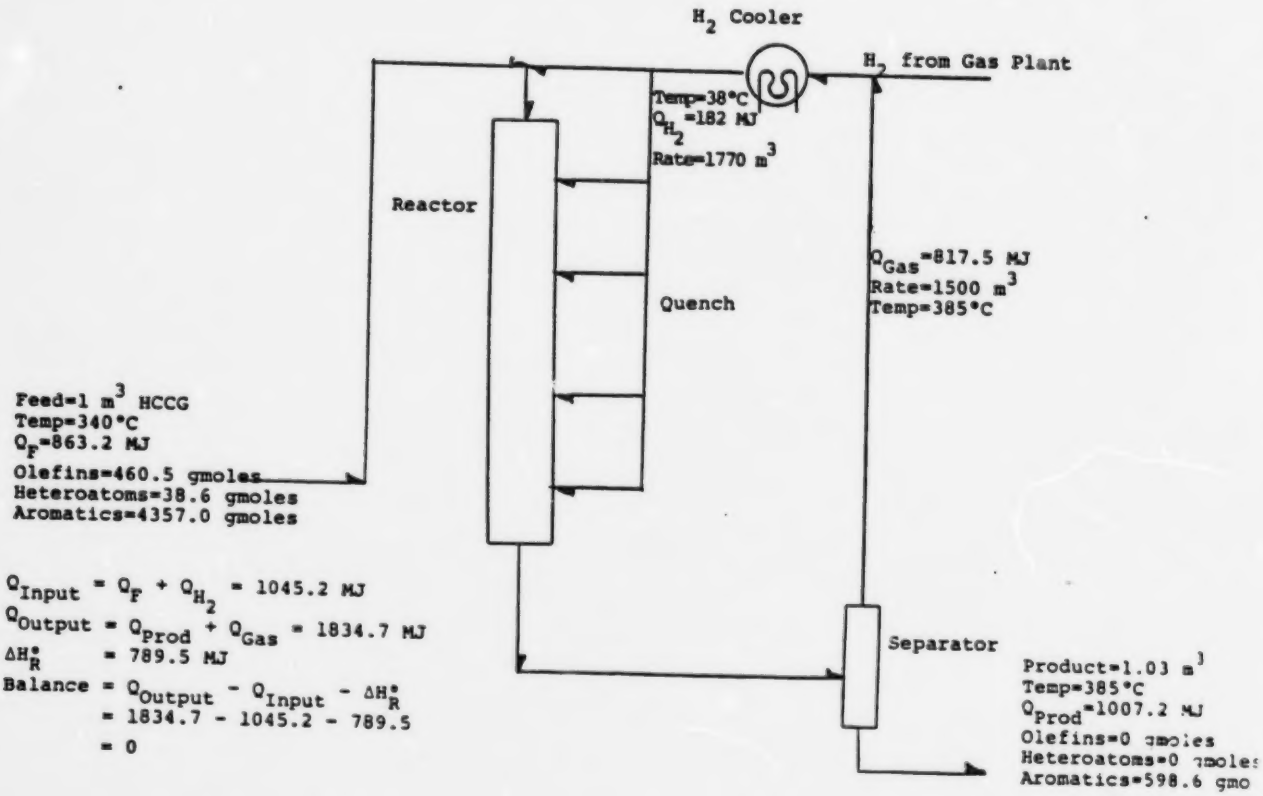


FIG. 4. 4. 4 SCREENING RUN PRODUCTS SMOKE PT. vs LHSV

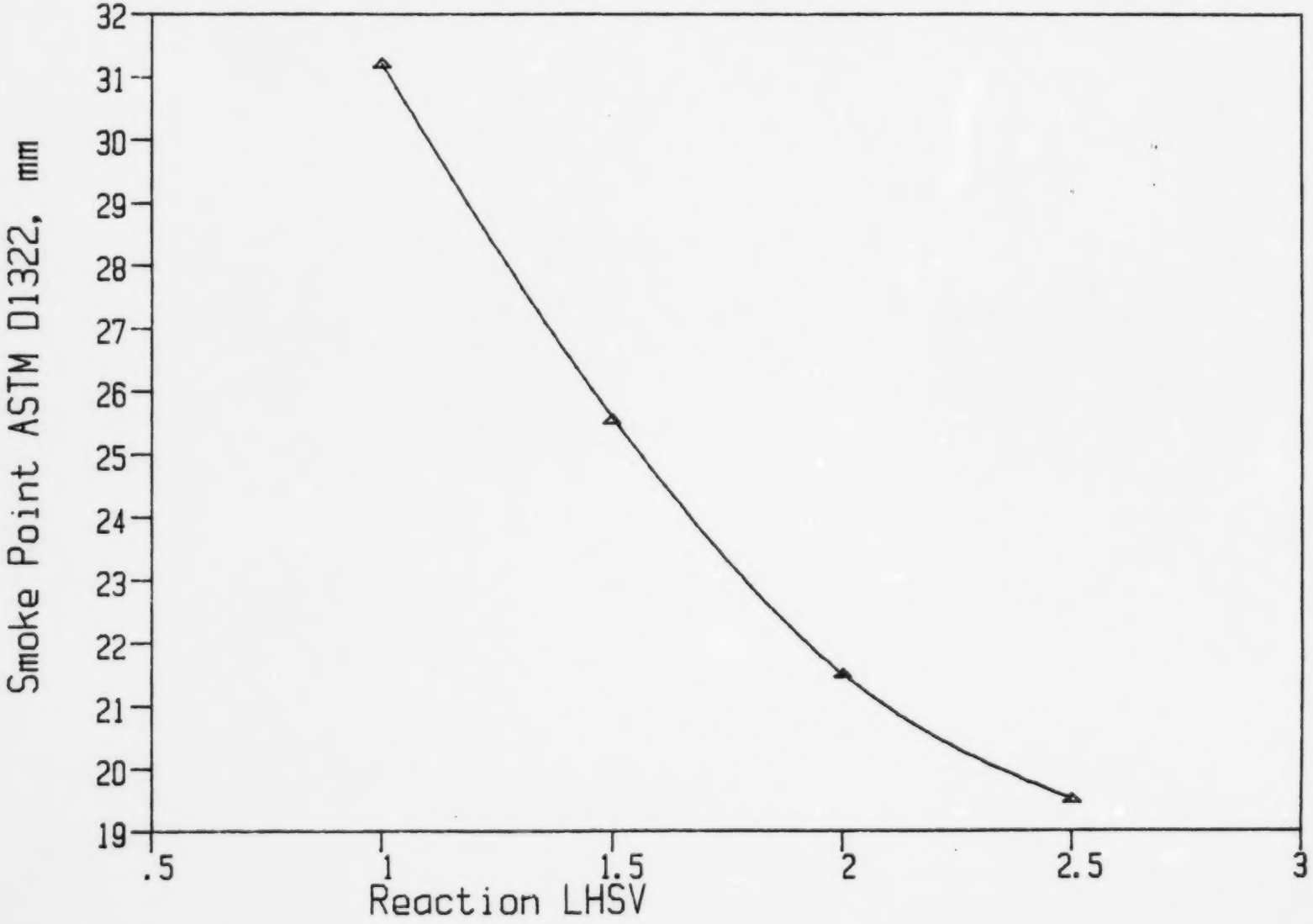
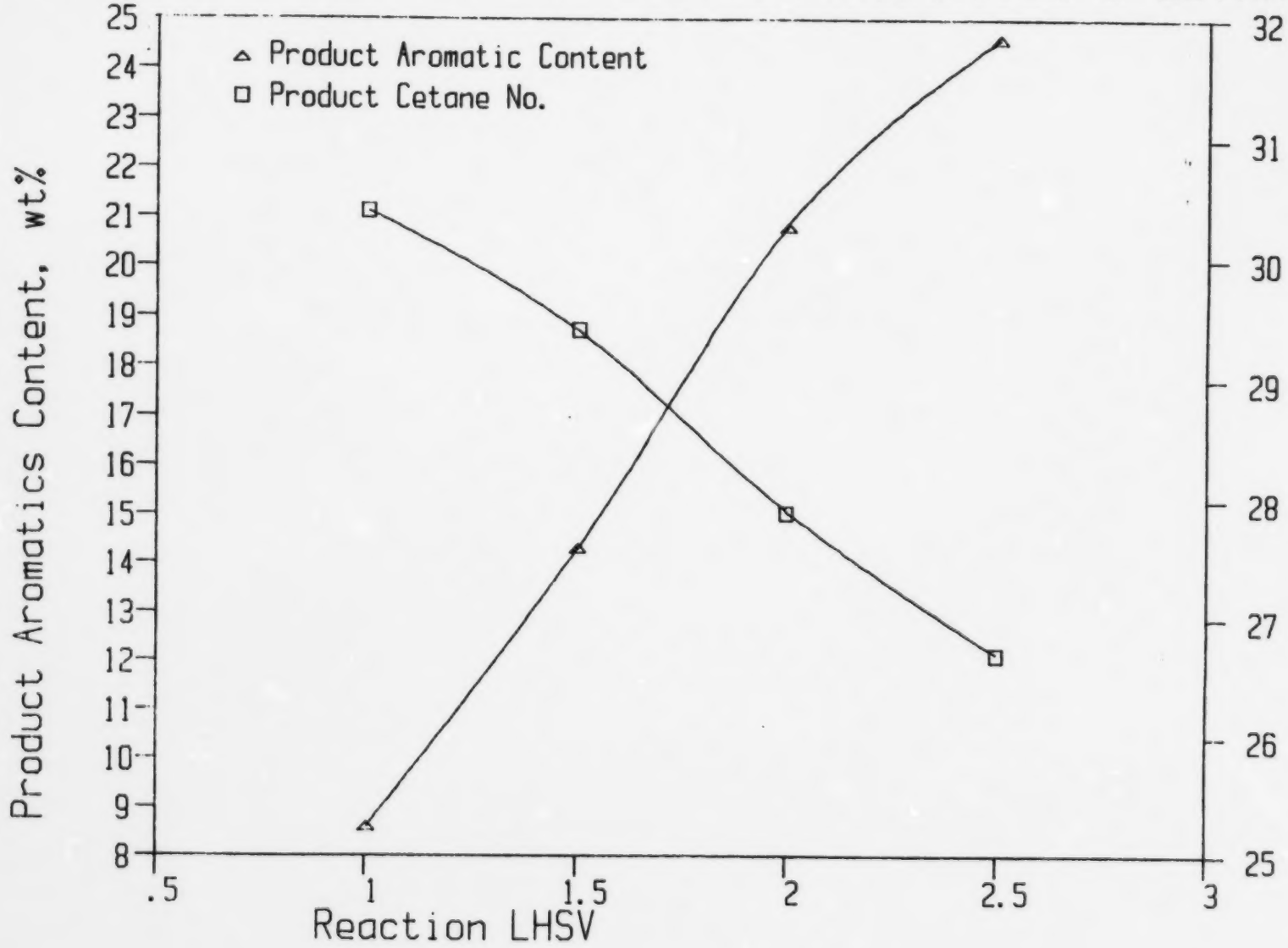


FIG. 4.4.5 EFFECT OF LHSV ON AROMATICS & CETANE NO.



APPENDIX

FOR INTER-OFFICE USE/POUR USAGE INTER-SERVICE

TO/À Distribution List

Project No.: 50-79
51-83-65

RESEARCH & DEVELOPMENT

December 14, 1983.

38.2° API GRAVITY INTERPROVINCIAL PIPELINE MIXED BLEND

(SAMPLE NUMBER: D83-81-A)

A B-2 semi-detailed crude oil evaluation was carried out on one drum of IPL Mixed Blend.

If you have any questions please contact H. Notzl at R&D.

HN:vs
Attach.

R.R. Deutscher,
FUELS PROJECTS

FOR INTER-OFFICE USE/POUR USAGE INTER-SERVICE

TO/À See Distribution List

File No.: 50-79
51-83-65

Research & Development
December 13, 1983

38.2 °API Gravity Interprovincial Pipeline Mixed Blend (Sample Number: D83-81-A)

A B-2 semi-detailed crude oil evaluation was carried out on a drum (D83-81-A) of Interprovincial Pipeline Mixed Blend (IPL). Sampled in July 1983 (L3SW-893). Logistics requested the evaluation for updating information.

1. CRUDE OIL

The Interprovincial Pipeline Mixed Blend crude is a 38.2 °API gravity intermediate type crude with a total sulfur content of 0.52 wt% and a mercaptan content of 203 ppm. The crude consists of 7.12 vol% light ends (C_2 to nC_6) and has the following K-factors and yields.

	U.O.P. K-factor	Yield Vol %
Light Straight Run Naphtha (15-75°C)	12.76	7.68
Heavy Straight Run Naphtha (75-195°C)	11.75	24.77
Atmospheric Distillate (195-360°C)	11.70	29.62
Gas Oil (360-535°C)	--	22.45
Residuum (535°C+)	--	11.77

2. NAPHTHAS (15-195°C)

The sulfur content of L.S.R.N. and H.S.R.N. are 0.06 wt% and 0.05 wt% respectively. The mercaptan content is 506 ppm for

L.S.R.N. and 182 ppm for H.S.R.N. The catalytic reforming yield predictions are similar to previous data on IPL crude.

3. ATMOSPHERIC DISTILLATE (195-360°C)

The yield of atmospheric distillate from the crude is 29.62 vol% with a 36.8 °API gravity and a sulfur content of 0.34 wt%. The cetane index of 50.4 indicates good diesel fuel combustion properties. The pour point (-24°C) and the cloud point (-15°C) show good low temperature operability.

4. GAS OIL (360-535°C)

The yield of gas oil from the crude is 22.45 vol% with a 24.9 °API gravity. The pour point is 36°C and the aniline point is 90.8°C.

5. RESIDUUM (535°C+)

The fraction of the crude that is residuum is 11.77 vol% with a 16.0 °API gravity. The sulfur content is 1.52 wt% and the nitrogen level is 4460 ppm.

HN/bp
Attach.

H. Notzl

GULF CANADA LIMITED

RESEARCH AND DEVELOPMENT DEPARTMENT

PAGE 1A

CRUDE IPL Mixed Blend

SAMPLE NO. D83-81-A

PROJECT NO. 51-83-65

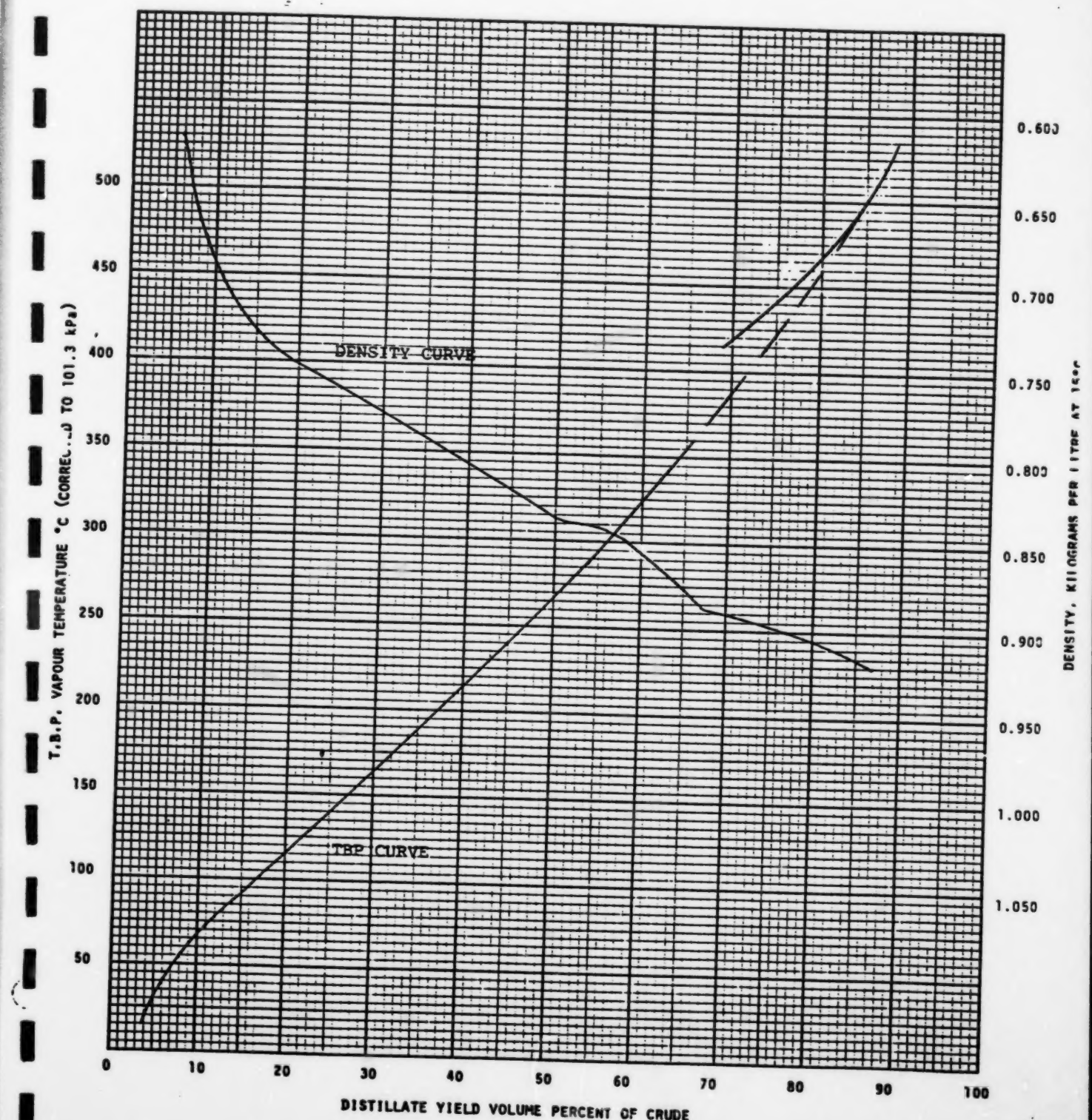
GRAVITY °API 38.2

SPECIFIC GRAVITY 60/60

DENSITY kg/L @ 15°C 0.8332

TRUE BOILING POINT CURVE

DENSITY MID % CURVE



B2 CRUDE OIL EVALUATION (SEMI-DETAILED)

CRUDE & PRODUCTS INSPECTIONS

CRUDE: IPL Mixed Blend
SAMPLE NO.: D83-81-A

STILL: 22.0 L & 6.0 L Hi Vac
OPERATOR:

DATE:

	METHOD REFERENCE	CRUDE	NAPHTHAS L.S.R.	NAPHTHAS H.S.R.	ATMOSPHERIC DISTILLATE	GAS OIL	RESIDUUM
Cut Range (TBP) °C			15-75	75-195	195-360	360-535	535+
Position in Crude From			3.71	11.39	36.16	65.78	88.23
% by Vol To			11.39	36.16	65.78	88.23	100.00
Yield % of Crude			7.68	24.77	29.62	22.45	11.77
Density @ 15°C	D1298/GCM 243	0.8332	0.6518	0.7616	0.8403	0.9045	0.9586
°API		38.2	85.6	54.2	36.8	24.9	16.0
RVP kPa	D323	26.9					
Rams. C. Res. %	D524	1.64				0.12	
Salt ppm	GCM 117	56					
B. S. & W. vol%	D96	0.30					
Cloud Pt. °C	D2500				-15	Too Dark	
Pour Pt. °C	D97	-15			-24	36	
Aniline Pt. °C	D611				68.7	90.8	
Viscosities:	D445 & D2170						
cSt @ 25°C		4.866					
cSt @ 40°C		3.413			2.869		
cSt @ 65°C						18.45	
cSt @ 100°C						6.809	356
cSt @ 120°C							118
cSt @ 135°C							65
Viscosity Index	D2270					78	
Penetration @ 25°C/0°C	D5						T.S./67
Sulphur %	XRF	0.52			0.34	0.76	1.52
	D1266		0.06	0.05			
Total Nitrogen ppm	D3431 (GCM 176)	(802)		<1		1005	(4460)
RSH ppm/H_2S ppm	GCM 118	203/12	506/16	182/-	67/-		
Cetane Index	D976				50.4		
Gr. Heat of Comb. kJ/kg	3.GPO(#23.4)	45,513					
Distillation							
IBP	D86 &	42 (-43)	24	96	210		
10%	(GCM 379)	106 (92)	34	108	228		
30%		192 (175)	41	118	244		
50%		290 (272)	48	132	267		
70%		375 (373)	56	148	293		
90%		(503)	66	167	319		
FBP		(622)	72	191	332		
Recovery %			96.1	99.7	98.6		
U.O.P. "K" Factor			12.76	11.75	11.70		
Light Ends Vol %	GCM 223						
C_2	(Crude)	0.13	—	—			
C_3		1.04	0.72	—			
iC_4	GCM 429	0.57	1.89	—			
nC_4	Distillate	1.97	10.95	0.07			
iC_5		1.43	17.01	0.08			
nC_5		1.98	23.98	0.18			
C_6^+		92.88	45.45	99.67			
PONA Vol %	GCM 162						
Paraffins			83.8	44.5			
Naphthenes			9.5	44.8			
Aromatics			1.7	10.7			
Olefins			*N/E	*N/E			
INCA Vol %	GCR 49						
Isoparaffins			38.8	22.9			
Normal Paraffins			50.0	21.6			
Cycloparaffins			9.5	44.8			
Aromatics			1.7	10.7			
Wax Content wt %	Gulf U.S. 281/69	3.37					
Metals, Nickel ppm	GCM 195	3.17					
Vanadium		4.04					
Copper		0.06					
Iron		2.65					

*N/E = Not Examined
Crude metals calculated from Red. Crude